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Studies on environmentally friendly flame retardants for cellulosebased materials

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Brandforsk

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The official project report, to which reference should be made, can be found on the LTU´s website.

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Preface

This report summarizes Brandforsk project 700-181. We are grateful for the financial support from Brandforsk, without which this study had not been possible.

We would like to thank the reference group: Mattias Delin from Brandforsk, Robert Jansson McNamee from Brandskyddslaget and Anders Lundberg from Swedish Civil Contingencies Agency (MSB). Our meetings have been very valuable with many different points of view and recommendations.

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We appreciate all the help we got from Tobias Sparrman, Umeå University, who helped us with the NMR analyses, and Alexandra Byström, LTU, for assistance with cone calorimetry experiments.

Abstract

Phosphorus based flame retardants are considered to be the best for cellulose-based materials such as cotton and wood. A non-toxic naturally occurring substance with high phosphorus content is phytic acid, which is used by plants as the main storage of phosphorus. It is prevalent in grains and seeds so we eat it every day. Phytic acid and phytate complexes with various common and non-toxic metal ions or ammonia have been studied on cotton and wood in order to systematically assess their performance as flame retardants and elucidate their mechanisms of action.

Simple combustion tests have been used to gain a first overview of the relative performance of the flame retardants depending on which ion is combined with the phytic acid, and in which proportions. Analytical methods such as TGA and calorimetry have been used to investigate the thermal properties and thermal degradation of the samples. Spectroscopic techniques such as MAS NMR have been used to explain the chemistry behind the thermal degradation mechanisms in molecular detail. The main focus has been on cotton samples, but an efficient methodology to control the humidity of wood samples in lab scale has been developed for future investigations on wood.

Phytic acid and its complexes have a flame retarding effect on both cotton and wood. The thermal process is similar on both materials. The mechanism is low-temperature charring giving less combustible degradation products, followed by cooling polymerization of the phosphate groups in the phytic acid, and formation of a second barrier to prevent the mixture of combustible volatiles and oxygen. It is important to have ionizable protons available in the flame retardant to induce the main mechanism of charring. Cone calorimeter tests on cotton samples show that the samples self-extinguish. Sodium phytates have a better performance than calcium phytates, as shown from combustion tests and FIGRA index on cotton samples. Possibly the superior flame retarding effect of sodium compared to the other ions is because of the radical quenching ability of alkali metals, but further investigations are needed into this issue.

Some of the results are also available in Bachelor and Master theses, and in a recently accepted paper in Green Materials Special Issue on Sustainable Flame Retardants.

The results may be of interest to the scientific community as well as for companies and organizations that work for a fire-safe and sustainable living environment.

Sammanfattning

Fosforbaserade flamskyddsmedel anses vara de bästa för cellulosabaserade material som bomull och trä. Ett icke-toxiskt naturligt förekommande ämne med högt fosforinnehåll är fytinsyra, som används av växter för lagring av fosfor. Det är vanligt i frön och sädesslag så vi äter det varje dag. Fytinsyra och fytatkomplex med olika vanliga och icke-toxiska metalljoner eller ammoniak har studerats på bomull och trä för att systematiskt bedöma deras prestanda som flamskyddsmedel och belysa deras verkningsmekanismer.

Enkla förbränningstester har använts för att få en första översikt över flamskyddsmedlets relativa prestanda beroende på vilken jon som kombineras med fytinsyran och i vilka proportioner. Analysmetoder såsom TGA och kalorimetri har använts för att undersöka provernas termiska egenskaper och termiska nedbrytning. Spektroskopiska tekniker såsom MAS NMR har använts för att förklara kemin bakom de termiska nedbrytningsmekanismerna på molekylär nivå. Huvudfokus har varit på bomullsprover, men en effektiv metod för att kontrollera fuktigheten i träprover i labbskala har utvecklats för framtida undersökningar av trä.

Fytinsyra och dess komplex har en flamskyddande effekt på både bomull och trä. Det termiska förloppet är liknande för bägge materialen. Mekanismen är lågtemperaturförkolning vilket ger mindre brännbara nedbrytningsprodukter, följt av kylande polymerisation av fosfatgrupperna i fytinsyran och bildning av en andra barriär som förhindrar blandning av brännbara flyktiga ämnen och syre. Det är viktigt att det finns joniserbara protoner i flamskyddsmedlet så att den huvudsakliga mekanismen förkolning kan initieras. Konkalorimetertester på bomullsprover visar att proverna är självsläckande. Natriumfytater fungerar något bättre än kalciumfytater, vilket framgår av förbränningstester och FIGRA-index på bomullsprover. Den överlägsna flamskyddseffekten hos natrium jämfört med de andra jonerna beror möjligen på den radikalfångande mekanismen hos alkalimetaller, men ytterligare undersökningar behövs i denna fråga.

En del av resultaten finns också tillgängliga i kandidat- och masteruppsatser, och i ett nyligen accepterat manuskript i Green Materials specialnummer om hållbara flamskyddsmedel.

Resultaten kan vara av intresse för det vetenskapliga samfundet såväl som för företag och organisationer som arbetar för en brandsäker och hållbar livsmiljö.

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1 Introduction

1.1 Background

Various environmental policy goals and instruments impose demands on a sustainable society. The requirements include, among other things, minimizing the use of energy and the use of renewable raw materials. One of the environmental quality goals that the Swedish government has set is that we should have a non-toxic environment [1]. This means, e. g., that dangerous substances must be replaced by less dangerous ones.

Natural materials (e.g., wood) have become interesting to use for buildings and textiles, both because it does not require as much energy to produce the products and because they are renewable. Many different natural textiles are cellulose-based, such as cotton and linen, and cellulose-based textiles can also be made from wood, e. g. viscose and lyocell.

Housing fires in Sweden kill on average about 120 people each year [2], and many more are injured. Many of these fires have arisen in loose furnishings (sofas, curtains, etc.). For loose furnishings, there are no government requirements for fire safety, but authorities (e. g. MSB, municipalities, county councils) try to set requirements for a fire-safe environment, among other things by proposing flame retardant products [3].

Today, there are hundreds of different flame retardants on the market and demand for flame retardant products is increasing. Many of these flame retardants have unfortunately proved harmful to both man and nature, so there is a desire from society to replace them with environmentally friendly and harmless ones. In particular, halogenated flame retardants such as brominated diphenyl compounds have been shown to be highly toxic and bioaccumulating, and have been banned or otherwise restricted in the US and the EU [1,4,6].

One step towards less hazardous flame retardants has focused on synthetic phosphorus-based compounds [4,5] and, although less toxic than halogenated flame retardants, sometimes dangerous chemicals are used in their preparation. In recent years, therefore, using bio-based substances as environmentally friendly flame retardants has been considered [7]. Many naturally occurring substances have properties that make them work well as flame retardants. They are non-toxic and their decomposition products are also non-toxic and waste does not need to be disposed of in any special way. They are also often relatively inexpensive to extract from the biomass.

One conceivable naturally occurring substance with the potential to act as an environmentally friendly flame retardant is phytic acid, also called inositol hexaphosphate. Phosphorus-based flame retardants have been found to be particularly effective for cellulose-based materials [4,8] and phytic acid contains 28% phosphorus, so it is of interest to develop the knowledge of this substance as flame retardant for wood and cotton. By mixing the phytic acid with various commonly occurring harmless salts (e. g. sea salt), all sides of the so-called fire tetrahedron can be eliminated at the same time as the material becomes water resistant.

1.2 Aim

The chemistry behind flame retardant mechanisms suggests that phytic acid should have the potential to function as an environmentally friendly flame retardant for cellulose-based materials. In this project, we have taken a deeper look into some previously reported and unreported results from our lab at Chemistry of Interfaces, Luleå University of Technology, and also performed some additional experiments, with the aim of explaining in detail the flame retarding behavior of phytic acid in combination with various metal ions applied on cotton and wood samples.

By applying chemical theories and analytical methods, we describe what happens to the flame retardant at different temperatures and how different combinations of ions affect the result. The macroscopic fire properties can thus be linked to the molecular properties of the flame retardant.

2 Theoretical background

2.1 Fire and flame retardants

The emergence of fires can be described with the fire tetrahedron, which is a development of the more common fire triangle [9]. In order for a fire to occur, four components need to be present in sufficient quantities: fuel, oxygen (or other oxidizing agent), heat and free radicals. Without radical formation, the reaction does not receive the rapid process (chain reaction) required for a fire. Flame retardants "attack" one or more of these components through various mechanisms [6,8,10,11]. The main mechanisms are to separate, cool, dilute or remove.

For solids, such as plastics, wood and cotton to ignite, their main constituents (polymers) must be broken down into smaller constituents. This is done through heating and the process is called pyrolysis. The higher the temperature, the more pyrolysis gases are produced and in the end the amount of pyrolysis gas in admixture with the air (oxygen) is sufficient for ignition to occur [6,10-12]. By separating oxygen and fuel, the combustible pyrolysis gases can be prevented from coming into contact with the oxygen in the air. This can be achieved by creating barriers, a dense surface layer that the pyrolysis gases cannot penetrate [8,10,11]. Flame retardants that create barriers are e.g. silicates or other polymer-forming agents. Another way to create a barrier is to char the surface. It has been found to be particularly effective for cellulose-based materials [6,8]. Carbonization is achieved by the formation of phosphoric acid which breaks down the cellulose molecules on the surface of the material into carbon and various fragments which are not as flammable as the usual pyrolysis gases. In addition, phosphorus-based flame retardants cause the carbonization to occur at temperatures below the ignition temperature of the pyrolysis gases, which further impedes ignition [8].

The most common extinguishing agent in the event of fire is water, as it absorbs large amounts of heat from the fire during evaporation. Many flame retardants absorb heat when they decompose to smaller constituents during heating [8,10,11]. Examples of such flame retardants are various salts, e.g. aluminum hydroxide which can be decomposed into alumina and water or magnesium carbonate which decompose to magnesium oxide and carbon dioxide. The solid oxides formed during the degradation form a barrier [11].

The gases formed during the decomposition of the flame retardant can also help to dilute the pyrolysis gases and the oxygen in the air closest to the surface, thus lowering the flammability.

By combining barrier-forming and gas-forming mechanisms, one can form a porous swollen surface layer (intumescence) that can isolate and dissipate heat [8,11,13]. A common substance that causes swelling is melamine which breaks down to ammonia gas and thus helps to inflate the barrier-forming substance.

A fourth flame retardant mechanism attacks the free radicals. The most effective substances in this category are the now banned halogenated agents, but an environmentally friendly substance in this category is common sea salt (sodium chloride). Alkali metals (e.g. sodium [14]) and halogens (e.g. chlorine), but also phosphorus [15,16], have the ability to capture and eliminate the radicals and then the fire process will slow down to eventually cease.

Flame retardants have been used for centuries and many of the chemicals still used to protect wood from fire were developed as early as the 19th century [8]. Most of the substances used as flame retardants have been various water-soluble salts that are not sufficiently resistant as they disappear if the material is exposed to moisture, e.g. during washing or wiping, or outdoors in rain [3,8]. Therefore, attempts have been made to develop a more resistant protection by combining substances that in different ways create an insoluble surface layer on the wood, e.g. phosphoric acid together with various nitrogen-containing resins. In addition, nitrogen and phosphorus have been shown to have synergistic effects [6,8,17]. The flame retardant must also not affect the underlying material [4].

2.2 Phytic acid

Phosphorus-based flame retardants have proven particularly effective on cellulose-based materials such as wood and cotton, and phytic acid (Figure 1) with the molecular formula $C_6H_6(H_2PO_4)_6$ has a high phosphorus content (28%). The structure consists of a cyclic hydrocarbon ring with a phosphate group attached to each carbon atom in the ring.

Phytic acid is formed by plants to store phosphorus which is an important nutrient and can be found in e. g. seeds and grain [18-21]. Phytic acid has been reported to be an antioxidant [19,20], it can prevent corrosion [20], it is believed to protect against many different diseases [22], and even to be able to fight cancer [19,22,23], among other things.

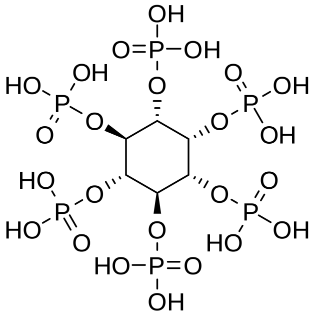

Figure 1. Phytic acid. Picture from Wikipedia.

A useful flame retardant must be resistant to abrasion and moisture when it has been applied to the material to be protected. Phytic acid is capable of forming very stable and poorly soluble complexes together with various metal ions (e. g. important nutrients such as zinc, calcium, magnesium, iron) [19]. These complexes, called metal phytates, have rendered phytic acid the name anti-nutrient as the important metals may not always be available for dietary uptake because of the strong complexation to the phytic acid; non-ruminant animals (humans, pigs and poultry) lack the necessary enzyme needed to digest the metal phytates. However, the strong bonds and the very low solubility allow permanent flame protection to be achieved by treating wood and cotton with suitable mixtures of phytic acid and harmless metal ions. In addition, no solvents other than water are needed.

Most of the phytic acid used today, e. g. in skincare products and in some medical applications, is extracted from agricultural waste where it is relatively easily accessible [20]. By utilizing the waste as a resource, the risk of local eutrophication by phosphorus leakage, e. g. from pig farms, is minimized.

The first study on phytic acid as a flame retardant was published in 2012 [24]. Subsequently, a number of further studies on flame retardancy of phytic acid in combination with other substances have been published, but only a few of these studies have been performed on cellulose materials (cotton) [24-31] and no study appears to have yet looked at phytic acid as a flame retardant for wood. The results show the potential of using phytic acid, but more extensive studies are needed to gain knowledge of how a phytic acid based flame retardant can be optimized to meet different fundamental conditions.

2.3 Cellulose

Cellulose is the main component of cotton and one of the main components of wood, the others being hemicellulose and lignin [6]. Cellulose is a polymer of glucose, while hemicellulose is oligomers of different sugars, and lignin is a crosslinked polymer keeping the plant structure together, see Figure 2. Depending on the species, the composition of the components may vary.

During heating, first unbound water is evaporated, below 100°C. Thereafter, the components start to decompose. First, the hemicellulose is degraded, thereafter the cellulose and finally the lignin, which is most stable due to its large three-dimensional network. To begin with, the structures are dehydrated (H and OH breaks off and form water, H_2O) and some charring occurs [6]. At higher temperatures, the components start to depolymerize, forming smaller combustible fragments. One component that forms during the depolymerization is levoglucosan, which is thought to be of major importance in fires [6,7,8,32]. Studies have shown that many flame retardants inhibit the formation of this compound, presumably by initiating dehydration and extended charring at a lower temperature, and thus hinder the depolymerization into levoglucosan and other combustibles [6,7,8,32].

Volatile components that break off from the structures are often richer in hydrogen and oxygen, leaving the nonvolatile part richer in carbon. This part polymerizes into polycyclic aromatic graphite-like structures, char. Flaming combustion can begin around 250°C if a pilot flame is present and approximately above 300°C, char forms rapidly as the pyrolysis intensifies. Above 500°C, no more volatiles form and the remaining material continues to smoulder [6].

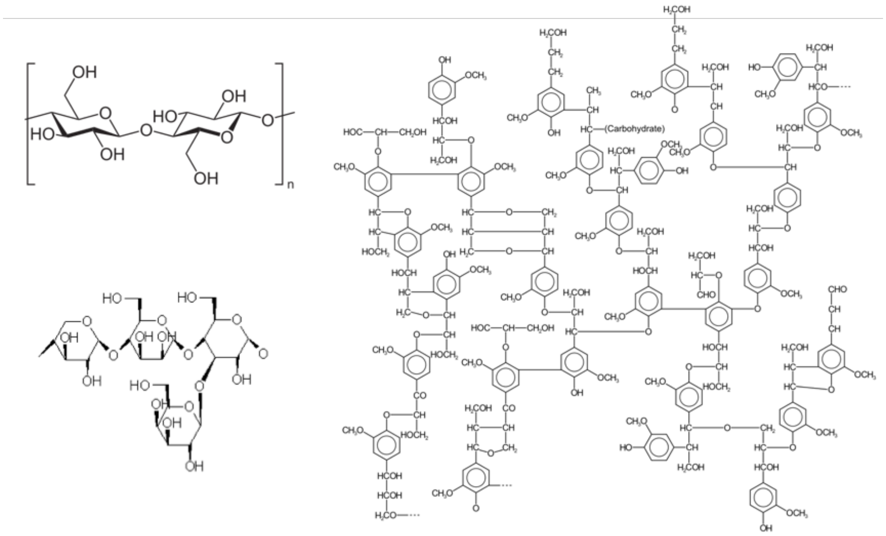

Figure 2. Top left: Cellulose. Bottom left: Hemicellulose. Right: Lignin. Pictures from Wikipedia.

3 Experimental methods

3.1 Sample preparation

3.1.1 Solutions

Ammonia or different metal salts of sodium, calcium, iron or aluminium were added in various amounts to aqueous solutions of phytic acid (1%, 3% or 10% w/w) according to the descriptions in Appendix 1 and in the references [33-36]. Table 1 lists the solutions used as flame retardants in this study.

The notation gives the relative molar ratio between additive and phytic acid. One mole of phytic acid ($H_{12}PA$) has in total 12 moles of ionizable hydrogens (two on each phosphate group, see Figure 1) which can be replaced by other ions. Samples refer to which materials have been treated with flame retardants. It is assumed that all added ions have been bound to PA in the same proportion they were added, and that they were adsorbed onto the material in the same ratio.

Table 1. Flame retardant solutions used in the study.

Solution	Notation	Sample*
1	$H_{12}PA$-3%	C, W
2	$(NH_4)_{12}PA$-3%	W
3	$(NH_4)_{12}PA$-10%	C
4	Na_6H_6PA-3%	C, W, S
5	Na_6H_6PA-10%	C, W
6	$Na_{12}PA$-3%	C, W
7	$Na_{12}PA$-10%	C
8	$Na_4Ca_2H_4PA$-3%	W
9	Na_4Ca_4PA-3%	C
10	Na_4Ca_4PA-10%	C
11	$Na_6Ca_2H_2PA$-3%	C
12	Ca_4H_4PA-3%	C, W
13	Ca_4H_4PA-10%	C
14	Ca_6PA-3%	W
15	$Ca_{0,5}H_{11}PA$-3%	C, W
16	$Fe_{0,3}H_{11}PA$-1%	S
17	$Al_{0,3}H_{11}PA$-3%	S

* C = Cotton; W = Wood (spruce); S = Wood sticks (ash)

Solutions 14, 15, 16 have very low solubility so only a tiny amount of metal ions could be added to the solutions to avoid precipitation of metal phytates in the beaker.

In addition, concentrated aqueous solutions of $H_{12}PA$, Na_6H_6PA and Ca_4H_4PA were freeze-dried in liquid nitrogen for three days until Na_6H_6PA and Ca_4H_4PA became solids. $H_{12}PA$ remained a semi-solid. The samples were then used for analytical tests.

3.1.2 Cotton samples

Fabrics of 100% cotton of standard quality were purchased from Ohlssons tyger in Luleå, in order to have more real life samples. The fabrics were washed in a washing machine and dried in hot air prior to the study, in order to remove any excess dye or other contaminants (e.g. remnants of bleach) that could affect the result. The results of an analysis of the dye content in different fabrics can be seen in Appendix 2.

The cotton was cut into pieces 3x10 cm^2 and then dipped once in the solutions for 1 minute according to Table 1. After the dipping, each set of samples were hung to dry in open air for 1, 2, 3, and 6 days, respectively, so that the effect of drying time on the results could be investigated. The cloth pieces were weighed before dipping, and prior to the burning to determine the amount of flame retardant that was absorbed [33,36]. Likewise, cotton pieces of dimensions 3x5 cm^2 were prepared for analytical tests. These samples were dried for two weeks. For cone calorimeter tests, cotton pieces 110x110 mm^2 were cut and treated with 3% flame retardant solutions. The samples were dried in air for at least three days.

3.1.3 Wood samples

Wooden planks of spruce were purchased from Beijer Byggmaterial, Luleå. They were cut in pieces 65x120x22,5 mm^3 and then dipped in the solutions according to Table 1. The number of dippings and the time of dipping varied between different sets of samples in order to study the effect of these two parameters. The pieces were weighed before dipping, and prior to the burning to determine the amount of flame retardant that was adsorbed [34].

Sawdust was produced from the wooden planks by machine polishing, and 8 grams of sawdust was mixed with the solutions for 10 minutes and then filtered and dried in open air. In addition, slivers of wood were carved from the bigger wooden pieces. These samples were used for analytical tests [34].

Wooden sticks of 6 cm length were made by removing the head of Solstickan safety matches (ash tree) purchased at Ica Porsön, Luleå. The sticks were dipped for 5 minutes, 1, 3, or 5 times, in the solutions according to Table 1 (Na_6H_6PA-3% only 1 dip) and thereafter left to dry in open air for approximately 24 hours [35].

Cubes with dimensions 2x1x1 mm^3 were made by cutting a match in pieces. The cubes were dipped in the solutions 1 or 5 times. Sawdust was produced by chopping the matches in tiny pieces. The sawdust was dipped once in the solutions. These samples were used for analytical tests [35].

3.1.4 Furnace treatment

To investigate what happens to the flame retardant during different stages in the thermal decomposition, samples were heated in porcelain crucibles inside a furnace to selected temperatures between 100°C and 1000°C. Samples investigated were sawdust and cotton with different flame retardants, as well as the pure flame retardants and a few calcium polyphosphate reference compounds.

The heating rate was 20°C/minute. The samples were kept at the target temperature for ten minutes (one hour for the pure flame retardants), and then allowed to cool down to room temperature.

3.2 Combustion tests

3.2.1 Butane burner

Cotton pieces treated with the different flame retardant solutions were hung from a horizontal iron wire mounted above a butane burner according to the description in [33,36]. The height of the flame was adjusted to 6 cm and the height between the cloth and the tip of the flame was 9 cm. A timer was started when the cloth was hung above the flame with the aim to measure the time to ignition. If the fabric did not start burning, it was removed after 5 minutes and the damage to the fabric, if any, was noted. Each combustion test was performed inside a fume hood and repeated three times.

Wooden sticks treated with the different flame retardant solutions were placed in a similar way above a butane burner according to the description in [35]. Here, the height of the flame was 12 cm. A timer was started when the stick was placed above the flame and the time to charring, ignition, and bending, respectively, were measured. Each combustion test was performed inside a fume hood and repeated four times.

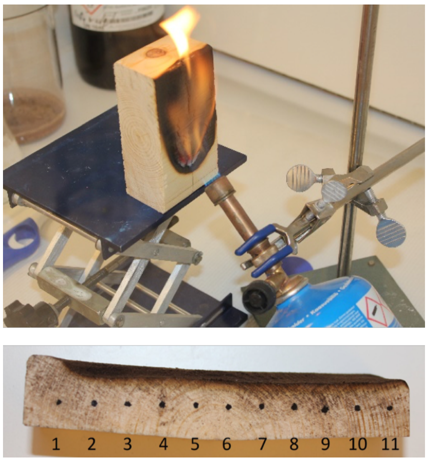

Figure 3. Top: Combustion test on wood. Bottom: Charring depth measurements [34].

Wooden pieces of spruce were exposed to a flame for 10 minutes by diagonal placement relative to the butane burner, see Figure 3 (top) [34]. Each combustion test was performed inside a fume hood and repeated three times. The charred residues were collected and the charring depth was measured at different points, see Figure 3 (bottom). Point 1 was at the edge closest to the burner.

3.2.2 Cigarette test

Many fire accidents are due to smoking in bed, where the smoker falls asleep and drops the burning cigarette on the clothes. A cigarette test was performed using an “artificial smoker”.

A low vacuum oil-free (to reduce the risk of fire spread) pump was employed to suck the smoke from a cigarette (Marlboro Gold). A non-flammable tube was used to connect the pump with the cigarette. A two-way valve was used to control the suction by the pump. A cigarette was mounted at the end of the tube and the pump was started. The suction from the pump simulates the drawings of breath from a smoker and the cigarette was ignited with a lighter.

Cotton pieces were put in contact with the burning cigarette to investigate the effect of treatment with different flame retardants.

3.3 Leaching and phytic acid determination

A good flame retardant has to be stable against humidity so it does not dissolve and the flame retarding properties are lost.

The amount of PA flame retardants that leach from a material can be determined by UV-Vis spectroscopy on the leachate. The absorbance of light is proportional to the amount of substance that absorbs the radiation so first a calibration curve with known concentrations of PA has to be made.

PA itself has very low absorbance so direct measurements of the UV-Vis signal requires very large amounts of PA to be detectable. In order to detect small concentrations of PA, the indirect method of using iron(III) thiocyanate was used instead by first making a calibration curve based on the absorbance of $Fe(SCN)_3$. PA binds strongly to iron(III), so the absorbance of $Fe(SCN)_3$ will decrease the larger the amount of PA was present in the solution [37]. Details about the UV-Vis calibration can be found in Appendix 3.

Cotton pieces treated with Na_6H_6PA-3% and Ca_4H_4PA-3% flame retardant solutions were put in 20 ml milliQ water in a capped glass bottle. The setups were placed on a shaking table for 10 minutes and thereafter, a 3 ml aliquot was withdrawn from the 20 ml leachate and transferred to a UV cuvette. 2.5 ml of $Fe(SCN)_3$ was added and the absorbance was measured using a UV spectroscope. The absorbance from the sample was correlated to the absorbance curve (Figure 3A in Appendix 3). From that value, the amount of PA leached from the cotton could be determined and compared to the original amount absorbed on the cotton.

3.4 Humidity control

The mass changes of the wood samples before and after treatment with the different flame retardants were very unreliable. In most cases, the masses became lower after treatment with flame retardant than before. One factor that can affect the mass of wood, and to a lesser extent also cotton, is differences in humidity from day to day. In order to get reliable data, it is important to control the humidity. Therefore, saturated salt solutions were used to construct efficient but convenient humidity chambers.

When a solute is present as a solid (in the pure phase) in contact with a solution, the solution is saturated. At any temperature, the concentration of a saturated solution is fixed and does not need to be regulated [38]. By providing excess solute, the solution will remain saturated.

A combined hygrometer and thermometer was placed inside a 5 liter glass chamber covered with a glass plate so that humidity and temperature could be monitored. The relative humidity inside the humidity chamber with only air present was measured during 24 hours and it was fairly constant at 33±1% and the temperature was 22°C.

100 ml of a saturated salt solution, see Table 2, was put in a 200 ml crystallizing dish and kept inside the humidity chamber. After a few hours, the chamber attained a stable humidity value. Pure water which gives 100% relative humidity was also used. The temperature was 22°C.

Table 2. Saturated salt solutions with different relative humidity.

Salt	Potassium acetate	Magnesium chloride	Magnesium nitrate	Sodium chloride	Potassium nitrate
Relative humidity	22%	33%	53%	74%	95%

1.000 g of sawdust (spruce) was put in a beaker covered with a watch glass to ensure that no dust can fall straight inside (but air can pass freely through the beak). The setup was kept inside an oven at 100°C for 16 hours, in order to ensure complete removal of moisture. The weight of the sample was recorded immediately after taking out from oven, and this weight was considered as the starting weight (referred to as the "zero humidity-zero weight increase").

The setup was then kept inside one of the humidity chambers for 24 hours and then the weight of the sawdust was recorded. After that, the setup was transferred to another humidity chamber, and kept for 24 hours, and the new weight was recorded. This process was repeated with all the relative humidities shown in Table 2. The increase in weight of any particular sample was calculated by subtracting the weight of the "zero sample". The humidity chambers were chosen in random order, in order to check the reproducibility of moisture absorption.

For comparison, the changes in weight of sawdust kept in open air, or in a vacuum desiccator, as well as sawdust dipped and stirred in water for 10 minutes and then dried in air, were also measured.

3.5 Thermal analyses

3.5.1 Thermal Gravimetric Analysis (TGA)

TGA was performed on the samples to investigate their decomposition and combustion processes. A small piece of the sample (1-2 mg) was put in the sample chamber and heated from 30°C to 800°C with a heating rate of 20°C/minute. The atmosphere was either air or nitrogen. During the heating, the weight of the sample was measured and the percentage mass loss as a function of temperature was plotted. For more details on the measurements, see [33-35].

3.5.2 Differential Scanning Calorimetry (DSC)

DSC was performed on the samples to detect the presence of endothermic and exothermic processes taking place during heating. The sample is placed inside a pan, and the sample and an empty reference pan are heated simultaneously in separate ovens and the difference in energy needed to keep the same temperature in both compartments is measured. The heating rate was 10°C/minute up to 350°C, and the atmosphere was nitrogen. For more details on the measurements, see [33,34].

3.5.3 Bomb calorimetry

Burning a substance in a bomb calorimeter gives information on its heat of combustion, i.e., how much heat is given away to the surroundings when the substance burns completely.

The bomb was filled with pure oxygen gas to a pressure of 30-35 atm and inserted into 2000 ml water. The temperature was allowed to equilibrate and then the sample, approximately 1 g of sawdust either untreated or treated with Na_6H_6PA-3%, $Fe_{0,3}H_{11}PA$-1% or $Al_{0,3}H_{11}PA$-3%, was ignited and complete combustion occurred. The temperature change of the water bath was measured and used to determine the amount of energy released. Benzoic acid was used as a reference to determine the heat capacity of the bomb calorimeter. For more details about the measurements, see Vikberg and Wagerland [35].

3.5.4 Cone calorimetry

With cone calorimetry, it is possible to get information on the combustion behavior of a material, e.g. how fast a sample ignites and burn, and how much heat is released in the process.

Blank untreated cotton samples were tested with 9, 14.9, 17 and 25 kW/m^2 of power in order to find the optimal power for the measurements. Too high power gives too fast burning and too low power does not give any ignition at all. Since the cotton samples were rather thin, 14.9 kW/m^2 was chosen as a suitable power to use.

The sample was placed in the sample holder and irradiated with the heat source until ignition. The time to ignition was measured. Once ignited, the heating was turned off and the time to flameout, i.e. the time it takes for the sample to either self-extinguish or burn completely was measured. The time of burning was calculated as time to flameout minus time to ignition.

The parameter FIGRA, Fire Growth Rate, is a way to express the fire properties. It predicts burning behavior of products compared to a reference material. FIGRA index has been determined by calculating the maximum heat release rate (HRR) divided by the elapsed time, and is a way to assess a fire based on the two facts that a large fire is more dangerous than a small fire, and a rapid fire growth is more dangerous than a slow fire growth [39].

3.6 Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR)

3.6.1 Background theory

When a sample is put inside a strong magnetic field, atomic nuclei in the molecules will interact with the magnetic field and start to precess like a gyroscope. The precession frequency depends on the magnetic field strength and on the type of nucleus, and can be detected from the perturbation of a radiofrequency pulse at the resonant frequency. Small differences in the closest environment around one atom relative to another in the same molecule give rise to slightly different precession frequencies, which can be detected as chemical shifts (in ppm) relative to a reference compound.

However, the precession frequency also depends on the orientation of a molecule relative to the magnetic field. In a solid, the molecules are distributed over all possible orientations leading to a broad band of overlapping signals from each nucleus giving no or very little information on the structural features of the molecule. To overcome this problem, the sample is spun at the magic angle (54,74° relative to the magnetic field). At this angle, most of the interactions are averaged out and the signals become much more narrow.

In order to understand the decomposition mechanism of the flame retardants, samples heated to different temperatures in a furnace (see Section 3.1.4) were investigated with MAS NMR. The high sensitivity of the method can give information on structural changes in the flame retardant occurring at specific temperatures, and whether these changes occur at different temperatures depending on the flame retardant and treated material in question.

3.6.2 Carbon-13

The most abundant carbon isotope, carbon-12, or ^{12}C, does not interact with a magnetic field, but carbon-13, ^{13}C, does. The ^{13}C isotope has only 1% natural abundance, so in order to increase the signal strength, energy from the more abundant protons (hydrogen-1 isotope, ^{1}H) is transferred to the carbon atoms (cross-polarization technique).

Solid state ^{13}C CP/MAS NMR spectra were recorded at 125.77 MHz on a Bruker Avance III 500 MHz spectrometer (B_0 = 11.7 T) with adamantane as an external reference (38.48 ppm relative to tetramethylsilane) [40]. Samples were packed in 4 mm zirconia rotors which were placed inside the magnetic field. The spinning speed was 10 kHz.

The phytic acid (PA) molecule contains six carbon atoms forming a ring and each carbon is bonded to one hydrogen atom and one phosphate group, recall Figure 1. Wood and cotton also contain rings of carbon atoms in their cellulose molecules, and in wood many other carbon containing substances are present as well. These signals will overlap with the signals from the carbon atoms in PA, so it is not possible to directly study the thermal degradation of PA on cotton and wood, but only as a pure compound.

3.6.3 Phosphorus-31

Phosphorus has only one isotope, phosphorus-31, or ^{31}P, with 100% natural abundance. The signal is strong so no cross-polarization is needed.

Solid state ^{31}P MAS NMR single-pulse spectra were recorded at 162.0 MHz on a Bruker Ascend Aeon WB 400 MHz spectrometer (B_0 = 9.4 T), and at 202.46 MHz on a Bruker Avance III 500 MHz spectrometer (B_0 = 11.7 T). Samples were packed in 4 mm zirconia rotors which were placed inside the magnetic field. The spinning speeds were 10 kHz (400 MHz spectrometer), and 14 kHz (500 MHz spectrometer) with solid $NH_4H_2PO_4$ as an external reference (0.9 ppm relative to 85% H_3PO_4) [41].

The phytic acid (PA) molecule contains six phosphate groups, one bonded to each carbon atom in the six-membered ring, see Figure 1. There are no phosphorus atoms in wood or cotton so in this case it is possible to study both the flame retardant itself, and the flame retardant adsorbed on sawdust or cotton.

4 Results and Discussion

4.1 Sample preparation

4.1.1 Room temperature samples

The cotton pieces were originally light green in color. After treatment with flame retardants, most pieces of fabric retained their appearance, but with 10% solutions they became a bit stiff. The fabric pieces treated with the most acidic solutions ($H_{12}PA$ and Ca_4H_4PA) turned brown after treatment with the flame retardant mixture [33]. Initially, this was interpreted as charring of the material due to the low pH. However, it turned out that after a few days of drying, excess acid evaporated and the fabric treated with Ca_4H_4PA-3% regained its light green color. The fabric color thus acts as a pH indicator.

Wood is not visibly affected by the flame retardant but the original wood color is retained, see Figure 4.

By weighing the test pieces before and after dipping into the flame retardant mixture, the amount of flame retardant adsorbed by the test piece could be estimated. For cotton, it was found that the mass of the test pieces increased by 10-15% for 3% solutions and by 27-38% for 10% solutions depending on the salt added [33,36]. This corresponds to approximately 70 to 100 µmoles for 3% solutions and 200 to 300 µmoles for 10% solutions, the higher values corresponding to the Ca_4H_4PA solutions, which have a higher affinity for the cotton because of lower solubility.

Figure 4. Wooden sticks dipped 1, 3 or 5 times in Na_6H_6PA-3%, $Fe_{0,3}H_{11}PA$-1% and $Al_{0,3}H_{11}PA$-3% [35].

It turned out that the weight of the pieces of wood and the wooden sticks varied too much with variations in the humidity, so it was not possible to judge how much flame retardant was bonded to the pieces of wood. However, it is evident from the tests carried out that flame retardants have been adsorbed.

The method of having all components of the flame retardant in the same solution was not so successful when using $Ca(OH)_2$ or $FeCl_3$ and $AlCl_3$. In these cases, the metal phytate started to precipitate at such low concentrations that it could not adsorb to the fabric or wood in a reasonable amount. Hence, the molar ratios metal:PA had to be kept below 1:1 in order to keep the components in solution until they had adsorbed to the material. In order to increase the metal:PA ratio, two separate solutions have to be used, one with PA and the other with the metal salt, and the material is dipped in the solutions separately, layer by layer.

4.1.2 Furnace treated samples

In order to understand the decomposition mechanisms of the flame retardants, the samples were heated inside a furnace to different temperatures, see Figure 5 and Section 3.1.4. Above 600°C there was no $H_{12}PA$ left, i.e, it has vaporized. Na_6H_6PA turned greyish at 500°C and become

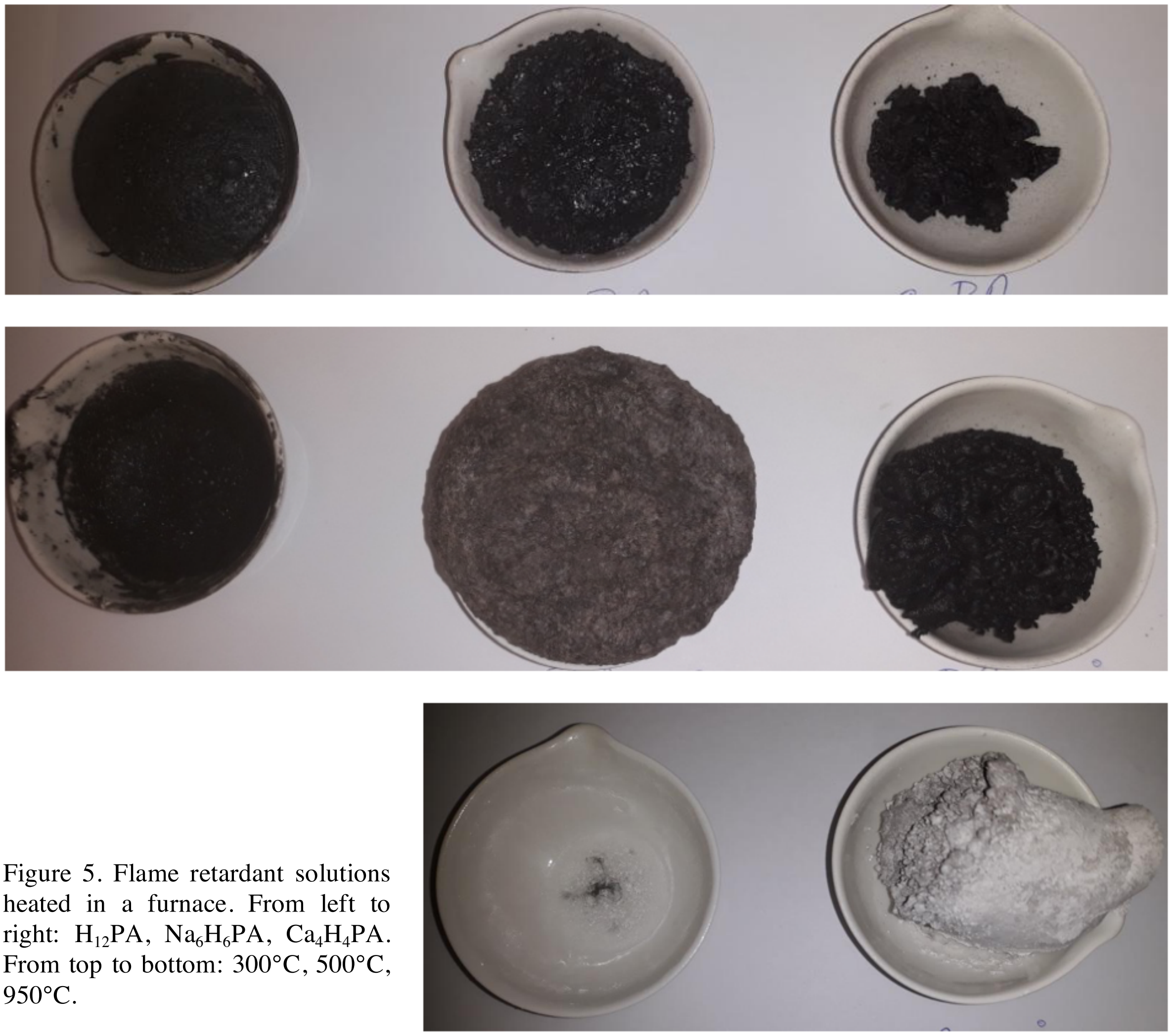

Figure 5. Flame retardant solutions heated in a furnace. From left to right: $H_{12}PA$, Na_6H_6PA, Ca_4H_4PA. From top to bottom: 300°C, 500°C, 950°C.

transparent and glassy at 950°C (difficult to see in the figure). Ca_4H_4PA samples stayed black up to 600 °C, then turned grayish. Ca_4H_4PA, and especially Na_6H_6PA, have intumesced at 500°C, possibly because of gas formation when some of the hydrocarbon part of the phytate combusts and form carbon dioxide and water vapor.

At higher temperatures, Na_6H_6PA decreases in volume, possibly due to melting, while Ca_4H_4PA has become very hard. The original colors of the samples at room temperature were light brown for Na_6H_6PA and brown for Ca_4H_4PA. The black color of the samples indicates that the hydrocarbon part of the phytate has started to char. The white color at higher temperatures, indicate that the carbon part has disappeared (burnt), leaving only the phosphate part.

4.2 Combustion tests

4.2.1 Cotton

Cotton pieces subjected to a butane flame for five minutes show varying degrees of charring depending on the flame retardant absorbed. Untreated cotton used as a reference material ignited after 5 seconds and burnt almost completely within a minute. Figure 6 shows examples of what the cotton pieces looked like. For a more detailed account of the appearance of the cotton pieces, see Kjellin [33].

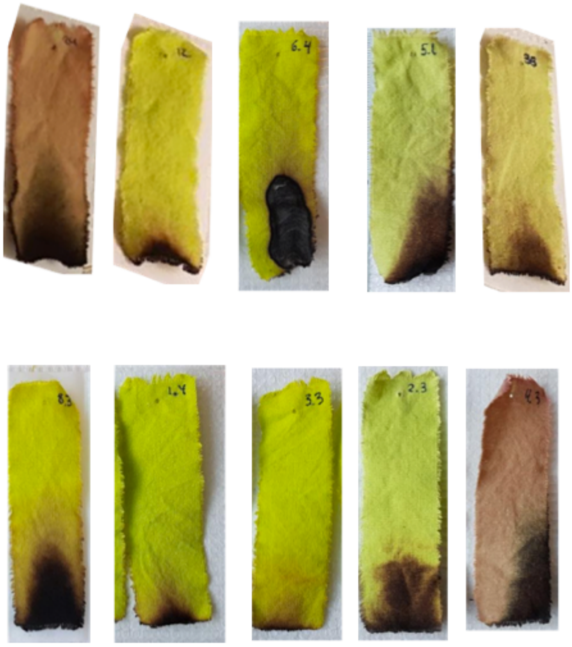

Figure 6. Cotton pieces subjected to a butane flame for five minutes. Upper row from left to right: $H_{12}PA$-3%, Na_6H_6PA-3%, $Na_{12}PA$-3%, Na_4Ca_4PA-3%, Ca_4H_4PA-3%. Lower row from left to right: $(NH_4)_{12}PA$-10%, Na_6H_6PA-10%, $Na_{12}PA$-10%, Na_4Ca_4PA-10%, Ca_4H_4PA-10%. Edited from [33].

The brown color of the fabric pieces exposed to the most acidic solutions ($H_{12}PA$-3% and Ca_4H_4PA-10%) arose already during sample preparation and is not a result of the combustion.

On the whole, 10% solutions provide better protection than 3% solutions, due to the fact that a greater amount of flame retardant has been absorbed onto the fabric, and sodium provides better protection than calcium. There is a small effect on the drying time for the cotton fabrics treated with Ca_4H_4PA solutions, the longer drying time gave slightly better protection [33].

4.2.2 Wood

Combustion tests on wood pieces (spruce) gave no clear results, both because of difficulties in controlling moisture content and thus determining the amount of flame retardant adsorbed, but also because the method of measuring charring depth did not give any significant differences between the sample pieces as it was difficult to control the height and intensity of the flame [34]. The forced convection of the butane burner caused irregularities in points 1-5 (Figure 3), but when the charring depth was measured only on points 6-11, wood pieces dipped three times in Ca_4H_4PA had a charring depth that was approximately half of the charring depth of untreated wood pieces, but considering the experimental difficulties it is not clear if this is a valid result.

Wooden sticks treated with $Fe_{0,3}H_{11}PA$-1%, $Al_{0,3}H_{11}PA$-3% and Na_6H_6PA-3% resist the flame better than untreated wood sticks. Figure 7 shows examples of what the wooden sticks look like after the combustion tests. The untreated sticks turn black within 20 seconds and then burn quickly while sticks treated with aluminum or sodium turn black after about 30 seconds and sticks treated with iron only after about 60 seconds. The treated sticks do not ignite, but continued heating from the flame causes the sticks to bend. It takes about 150 seconds for aluminum-treated sticks to bend, while sticks treated with iron or sodium bend after about 100 seconds. There is no significant trend in results between the number of dips in the flame retardant solution. The wooden sticks treated with

Figure 7. Wooden sticks treated with different flame retardants and subjected to a combustion test. From left to right: $Al_{0,3}H_{11}PA$-3%, $Fe_{0,3}H_{11}PA$-1% and Na_6H_6PA-3%. All sticks were dipped once in the solution. Edited from [35].

Na_6H_6PA-3% appear to be more affected than the other sticks. For more detailed reporting, see Vikberg and Wagerland [35].

It is interesting that wooden sticks treated with $Fe_{0,3}H_{11}PA$-1% has such a high resistance to the flame considering that this solution is only 1% compared to 3% for the other solutions. Due to the problems described in controlling the moisture, it was not possible to determine how much flame retardant is adsorbed on the wooden sticks, but the results from cotton show that more flame retardants are adsorbed the higher the concentration is and it seems reasonable to assume that the same applies to wooden sticks.

4.2.3 Cigarette test

As described in Section 3.2.2, a pump was used to ignite the cigarette. In the first test, when the cigarette was glowing, the pump was switched off, and the cigarette was put on the cotton piece. As not even the untreated cotton was very affected by this, because the cigarette glow was obviously not hot enough, and/or the table on which the cotton piece was placed had inappropriate thermal conductivity and heat capacity properties, new tests were performed where the pump was kept on for the whole time to keep the cigarette constantly hot.

Figure 8 shows a few selected results from these tests. The cigarette burns a hole through the untreated cotton in 10 seconds. The treated cotton pieces do not get burnt through even after 30 seconds, although the fabric becomes thinner. From the figure, it seems that $Na_6Ca_2H_2PA$ gives slightly better result than Na_4Ca_4PA, but overall the results for all PA flame retardants are similar. The methodology needs development, as it was difficult to keep the cotton piece and the cigarette in exactly the same positions during all the experiments.

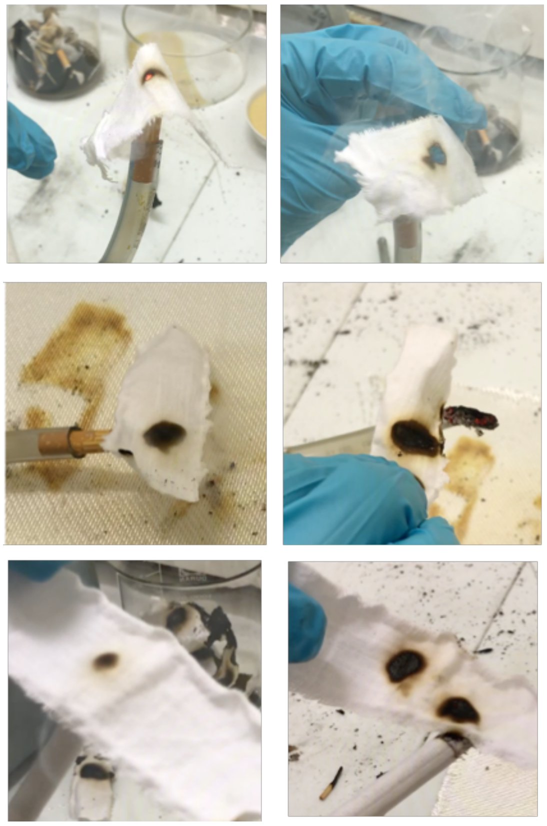

Figure 8. Cotton pieces in contact with a burning cigarette. From top to bottom: Untreated, Na_4Ca_4PA, $Na_6Ca_2H_2PA$. Left: After 6 seconds, Right: After more than 6 seconds.

4.3 Leaching and phytic acid determination

As described in Appendix 3, the amount of flame retardant that has leached from cotton was determined by UV-Vis spectroscopy.

The absorbance from the samples were correlated to the calibration curve (see Figure 3A in Appendix 3). The leachate (3 ml) from a 30 mg cotton piece treated with Na_6H_6PA-3% contained 98 μM PA, which corresponds to 1.56 mg Na_6H_6PA in 20 ml leachate, see Section

3.3. Assuming that the amount of Na_6H_6PA absorbed in the cotton is 12% [33,36], then the mass of the flame retardant leached is 43%.

No detectable amount of PA was leached from the cotton piece treated with Ca_4H_4PA-3%.

4.4 Humidity control

Sawdust that was kept on a table at room temperature in a beaker covered with a watch glass did not lose or gain weight significantly during 1-3 days (weight checked time to time). The relative humidity in the lab was apparently stable around 33% during the test period (see Section 3.4).

Sawdust kept over dehydrating agents (e.g. freshly charged silica gel, or anhydrous $CaCl_2$) inside a glass desiccator under mild vacuum for 3 days lost 2-3% of the original weight.

Sawdust kept inside an oven at 100°C for 1, 3, 8 and 16 hours lost 13% of the weight. All weight loss occurred during the first hour and after that the weight was constant. If this sample is kept in open air at room temperature, after a few minutes it regains its original weight, as shown in Figure 9.

Figure 10 shows the changes in mass of the sawdust compared to the sample weight fresh from the oven for various relative humidities according to Table 2. The process can be repeated over many cycles, the plot shows the values for two samples.

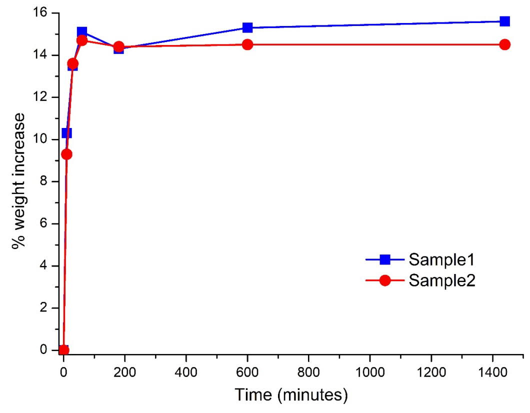

Figure 9. Moisture absorption rate of oven-dried sawdust when kept in air at room temperature.

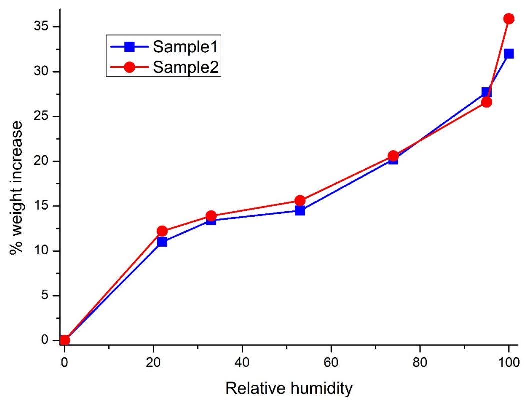

Figure 10. Weight variation of sawdust at different relative humidity.

Sawdust that was dipped and stirred in water for 10 minutes, and then dried in air for 1-3 days, shows 4-5% weight loss compared to the starting weight (before water dipping). This weight loss can be attributed to loss of water soluble minerals present in wood, and can explain the strange results for the wood samples in this study, where the wood samples dipped in aqueous solutions of flame retardants weighed less than the untreated wood samples.

If the water-dipped and air-dried samples were then placed in an oven at 100°C, the additional weight loss became 17%, to compare with the 13% weight loss of the sample that had not been dipped in water before put in the oven. The differing 4% is from extra water that was absorbed inside the pores after the minerals (8%) had dissolved.

It is clear that the humidity can be controlled very precisely, so for future investigations on flame retardants on wood samples this will be a convenient way to maintain reproducibility of the results. However, the most important factor seems to be the leaching of water soluble minerals from the wood samples during dipping in water, which decreases the mass of the sample, and prevents a correct determination of the mas flame retardant adsorbed. This parameter seems to be controllable as well.

4.5 Thermal analyses

4.5.1 Thermal Gravimetric Analysis (TGA)

Figure 11 shows examples of degradation processes in nitrogen atmosphere for untreated cotton and cotton treated with phytic acid solutions [33].

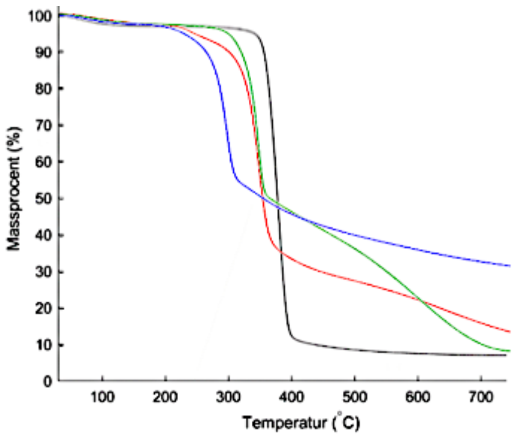

Figure 11. TGA on cotton pieces in nitrogen atmosphere. Black – untreated, Blue – $H_{12}PA$-3%, Green – Na_6H_6PA-3%, Red – Ca_4H_4PA-3%. Edited from [33].

All samples contain a few percent bound water that evaporates around 100°C. The untreated cotton decomposes only to a small extent before about 350°C, thereafter an almost complete pyrolysis occurs just before 400°C, leaving a residue of about 12%. Cotton treated with phytic acid ($H_{12}PA$) begins to lose mass already at about 200°C and has lost about half of the mass before 400°C. Thereafter, further pyrolysis follows so that at 700°C, about 31% of the mass remains. Also, cotton treated with Na_6H_6PA and Ca_4H_4PA begin to pyrolyze at a lower temperature than untreated cotton. Cotton with Ca_4H_4PA loses a greater proportion of its mass before 400°C than does cotton with Na_6H_6PA. On the other hand, the mass losses at higher temperature are greater for cotton with Na_6H_6PA than for cotton with Ca_4H_4PA.

Figure 12 shows examples of the degradation of cotton in air depending on the flame retardant treatment received. More examples can be found in Kjellin [33]. Again, the samples contain some % water that evaporates around 100°C. Like in the nitrogen atmosphere, treated cotton begins to lose mass at lower temperatures than untreated cotton. The fact that the decomposition starts at a lower temperature is considered to favor the formation of less flammable pyrolysis gases [8,32].

Unlike untreated cotton which loses about 90% of its mass below 400°C, the mass losses of the treated cotton samples stay below 50% at the same temperature. The early degradation of the flame retardant has probably contributed to charring of the surface of the cotton so that further pyrolysis is made more difficult.

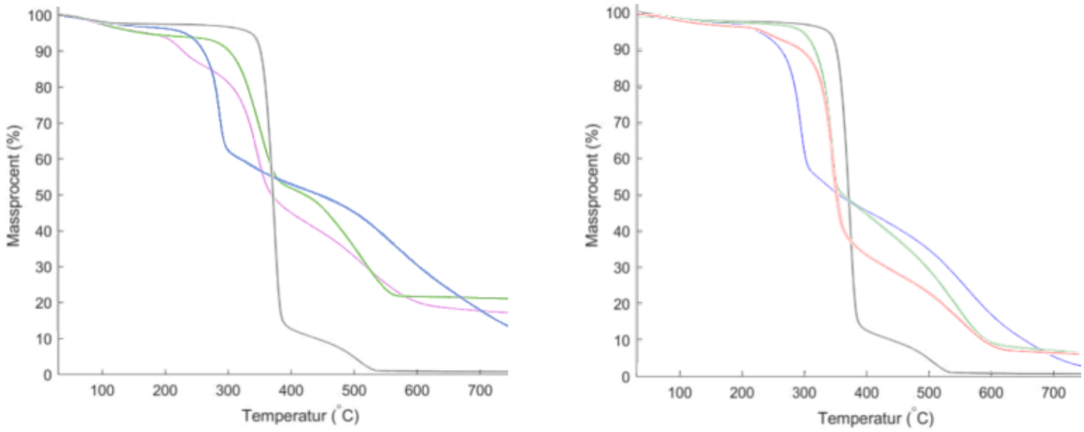

Figure 12. TGA on cotton pieces in air. Left: Black – untreated, Green – $Na_{12}PA$-10%, Blue – $(NH_4)_{12}PA$-10%, Pink - Ca_4H_4PA-10%. Right: Black – untreated, Green – Na_6H_6PA-3%, Blue – $H_{12}PA$-3%, Red - Ca_4H_4PA-3%. Edited from [33].

Cotton treated with $(NH_4)_{12}PA$-10% loses 40% of its mass already around 250°C. This is because ammonia (NH_3) evaporates, leaving $H_{12}PA$. The further decomposition of cotton with $H_{12}PA$ is very slow, and the mass loss is very small between 300°C and 500°C. TGA of cotton treated with $H_{12}PA$ in nitrogen atmosphere (Figure 11) also loses very little mass in this temperature range. $H_{12}PA$ contains a larger % of phosphate than the other flame retardants (because H atoms weigh much less than the metal ions) so the amount of phosphoric acid available for charring is larger, which may increase the charring and decrease/delay the pyrolysis.

In air, oxygen is available so the sample can ignite after pyrolysis. It is seen as a second mass loss after 400°C which is lacking in nitrogen atmosphere. In air, the remaining residues ignite and are burnt so that at a temperature just above 500°C, the untreated sample has burnt completely. At that temperature, between 20-40% of the mass is still left for the treated samples.

At 800°C, when the tests were stopped, 11% of cotton treated with $(NH_4)_{12}PA$-10% was left and around 20% of cotton treated with $Na_{12}PA$-10% and Ca_4H_4PA-10%, respectively.

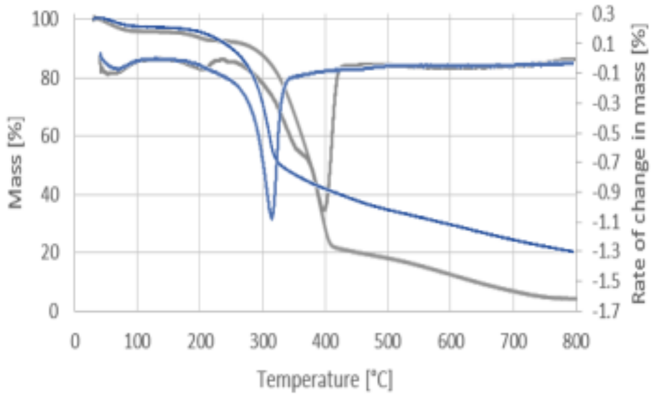

Figure 13. TGA curves and their derivatives for untreated sawdust (grey) and sawdust treated with $H_{12}PA$-3% (blue). Nitrogen atmosphere. Edited from [34].

For corresponding samples of 3% solutions, about 5% of the mass is left at 800°C, 10-30% at 500°C and approximately 40-50% just below 400°C [33].

Sawdust (spruce) treated with 3% flame retardant solutions showed similar results as cotton. Figure 13 shows the two extremes in nitrogen atmosphere. Sawdust treated with $H_{12}PA$-3% decomposes at the lowest temperature (maximum mass loss close to 300°C), and untreated sawdust at the highest (maximum mass loss close to 400°C). All other samples lie in between. Less than 5% of untreated sawdust remains at 800°C while 20% of sawdust treated with $H_{12}PA$-3% remains [34]. Compared to cotton (Figure 11), the onset of the pyrolysis starts at a lower temperature for sawdust than for cotton, and the process is slower, needing a larger temperature range to be completed. Cotton treated with $H_{12}PA$-3% retain more of its mass than sawdust treated with $H_{12}PA$-3%, but the amount of $H_{12}PA$-3% adsorbed on the sawdust is probably smaller.

In air, both slivers and sawdust were investigated by TGA. Slivers were dipped in Na_6H_6PA-3% and Na_6H_6PA-10% solutions for various lengths of time (up to 24 h), but there was no significant difference between the TGA curves. There was no significant difference between the TGA curves of slivers and sawdust treated with Na_6H_6PA either. The first decomposition occurs at slightly lower temperature than untreated wood, and more of the mass is retained at 500°C when the untreated wood has been completely combusted. At 800°C, less than 5% of the material is left for the treated sawdust.

Figure 14 shows examples of TGA curves in air for a few samples of sawdust. All flame retardants lower the decomposition temperature compared to untreated sawdust. Sawdust treated with $H_{12}PA$-3% decomposes at the lowest temperature. Sawdust treated with Ca_4H_4PA-3% loses more mass than sawdust treated with $Na_{12}PA$-3% before 400°C, but between 400°C and 500°C the sawdust treated with $Na_{12}PA$-3% loses the rest of its mass while sawdust treated with Ca_4H_4PA-3% has not lost the rest of its mass until at approximately 650°C. This same behavior can be seen also for the cotton samples [33]. In all cases, less than 5% of the mass remains at 800°C [34].

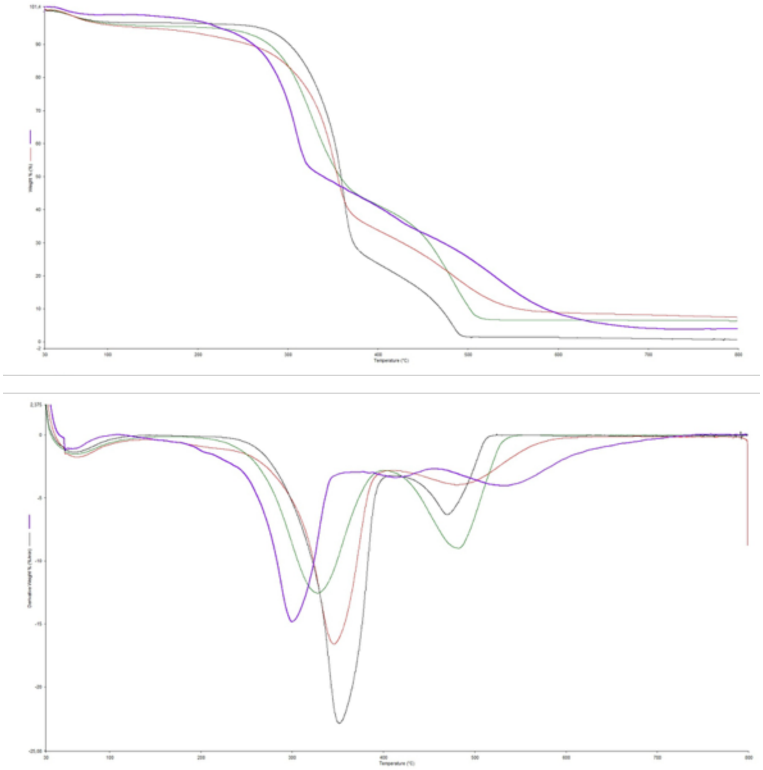

Figure 14. TGA curves (Top) and their derivatives (Bottom) in air atmosphere. Black: Untreated sawdust, Purple: sawdust treated with $H_{12}PA$-3%, Green: sawdust treated with $Na_{12}PA$-3%, Red: sawdust treated with Ca_4H_4PA-3%, Edited from [34].

The pyrolysis in nitrogen atmosphere of small wooden cubes (ash) without flame retardant leaves around 15% of the mass at 800°C, see Figure 15 [35]. The pyrolysis starts at a lower temperature compared to spruce (Figure 13), and also leaves a larger residual mass.

Small wooden cubes dipped once in Na_6H_6PA-3% decompose at the same temperature as the untreated cubes (onset below 300°C) and around 20-25% of the mass is preserved at 800°C, see Figure 15 and more data in Vikberg and Wagerland [35]. With five dips in the solution, more than 30% of the mass was preserved. Cubes dipped once in solutions of $Fe_{0,3}H_{11}PA$-1% and $Al_{0,3}H_{11}PA$-3% start to decompose at lower temperature (slightly above 200°C) and keeps around 30% of the mass at 800°C, Al slightly more than Fe. There is no difference for cubes dipped five times in $Al_{0,3}H_{11}PA$-3%, but for $Fe_{0,3}H_{11}PA$-1%, the TGA curve is identical to the one for $H_{12}PA$-3% (see Figure 13) [35].

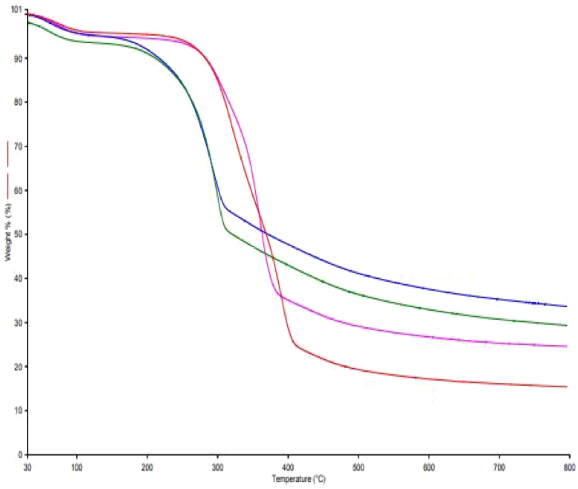

Figure 15. TGA curves in nitrogen atmosphere. Red: Untreated sawdust, Blue: sawdust dipped once in $Al_{0,3}H_{11}PA$-3%, Green: sawdust dipped once in $Fe_{0,3}H_{11}PA$-1%, Pink: sawdust dipped once in Na_6H_6PA-3%. Edited from [35].

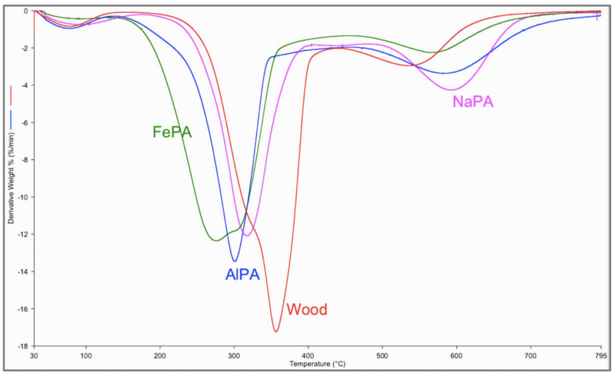

Figure 16. Derivatives of TGA curves in air atmosphere. Red: Untreated wooden cubes (ash), Blue: sawdust dipped once in $Al_{0,3}H_{11}PA$-3%, Green: sawdust dipped once in $Fe_{0,3}H_{11}PA$-1%, Pink: sawdust dipped once in Na_6H_6PA-3% [35].

In air, all samples decompose at a lower temperature than the untreated cubes, see Figure 16. The cubes treated with iron has a broader temperature range during which the main mass loss takes place, i.e. the first mass loss is slower. At 450°C both untreated cubes and cubes treated with $Fe_{0,3}H_{11}PA$-1% has lost the same amount of mass (around 80%). At this temperature, cubes treated with $Al_{0,3}H_{11}PA$-3% and Na_6H_6PA-3% both have around 40% of their masses left, Na slightly more than Al. At 800°C, around 10% of the mass is left for cubes treated with Na_6H_6PA-3%, and only a few % of the other cubes. The results for cubes dipped five times in the flame retardant solutions are similar, but slightly larger masses are left at 800°C [35].

TGA on the flame retardants themselves are shown in Figure 17. There is almost no difference between the curves for nitrogen and air atmosphere, except for $H_{12}PA$ which loses more mass in air than in nitrogen. This shows that the oxygen has an effect on $H_{12}PA$ above 400°C.

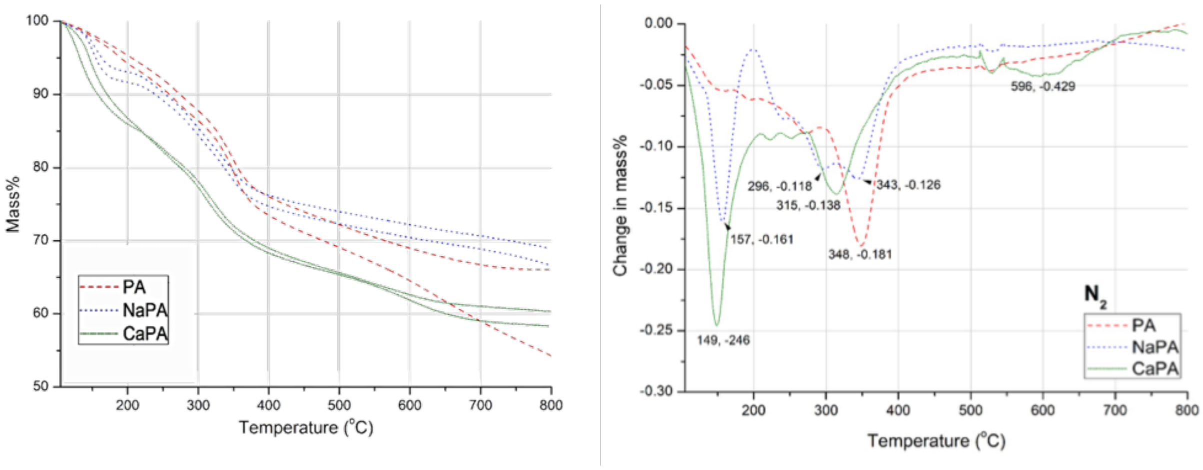

Figure 17. TGA curves (left) and their derivatives (right) of pure flame retardants. Red: $H_{12}PA$, nitrogen atmosphere (upper) and air (lower), Blue: Na_6H_6PA, nitrogen atmosphere (upper) and air (lower), Green: Ca_4H_4PA nitrogen atmosphere (lower) and air (upper).

Both Ca_4H_4PA and Na_6H_6PA lose mass at a high rate around 100°C. This is water that evaporates. The water in $H_{12}PA$ is more strongly bonded so it is removed over a larger temperature interval. The second mass loss, which is from the main pyrolysis, occurs slightly above 300°C, highest for $H_{12}PA$ (closer to 350°C). In all cases, more than 50% of the mass is left.

Figure 5 shows the appearance of the flame retardants after being heated to different temperatures. The samples at 300°C and 500°C have turned black from their original brownish colors, which shows that the material has polyaromatized into a graphite-like carbon material. At 950°C, the material is white. At this temperature, all carbon has combusted, leaving only the inorganic part. The mass loss occurs as gases, which expand the material as they blow through the solid part.

4.5.2 Differential Scanning Calorimetry (DSC)

Figure 18 shows exothermic and endothermic processes taking place during the first stage of thermal decomposition of a few cotton samples treated with different flame retardants. More samples can be found in Kjellin [33].

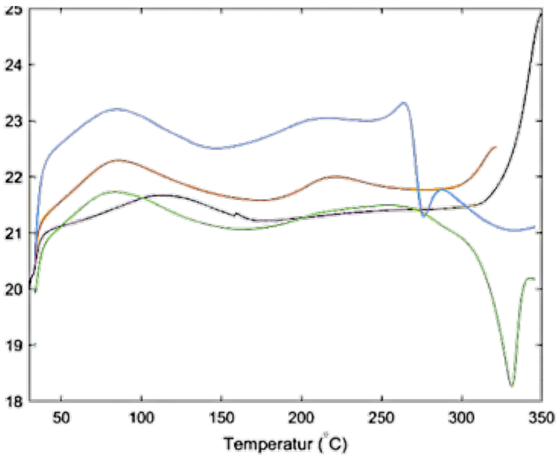

Figure 18. DSC curves on cotton pieces in nitrogen atmosphere. Black – untreated, Green – Na_6H_6PA-3%, Blue – $H_{12}PA$-3%, Red - Ca_4H_4PA-3%. Edited from [33].

In all cases, endothermic evaporation of water is taking place below 100°C (the curve goes up). Thereafter, all samples experience similar small exothermic (the curve goes down) and endothermic processes up to approximately 250°C The processes are not connected to any specific mass losses in the TGA curves (Figure 11). The thermal degradation of untreated cotton is very endothermic (breaking of chemical bonds) and takes place after 320°C. This is in accordance with the TGA results (see Figure 11), in which the thermal decomposition of untreated cotton starts at approximately this temperature.

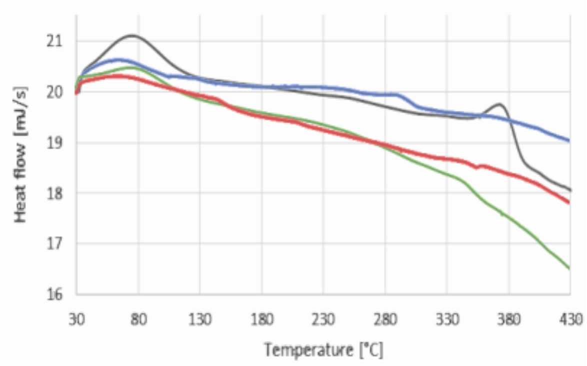

Figure 19. DSC curves on sawdust (spruce) in nitrogen atmosphere. Black – untreated, Green – Na_6H_6PA-3%, Blue – $H_{12}PA$-3%, Red - Ca_4H_4PA-3%. Edited from [34].

The samples treated with flame retardants start to degrade at lower temperatures, according to TGA (Figure 11), and it seems that for cotton treated with $H_{12}PA$-3% and Na_6H_6PA-3%, this decomposition is correlated with an exothermic process, while cotton treated with Ca_4H_4PA-3%, which according to TGA, decompose at the same temperature as Na_6H_6PA-3%, shows an endothermic beginning. Unfortunately, the Ca_4H_4PA-3% sample was only run up to 320°C, so it is not clear what happens after that.

Figure 19 shows the DSC results of wood (spruce) samples treated with flame retardants. The results are very different from the results on cotton. First of all, the heat flows are generally smaller. There is a very small endothermic degrading of the untreated wood at approximately 370°C, all other processes are exothermic, especially the pyrolysis of sawdust treated with Na_6H_6PA.

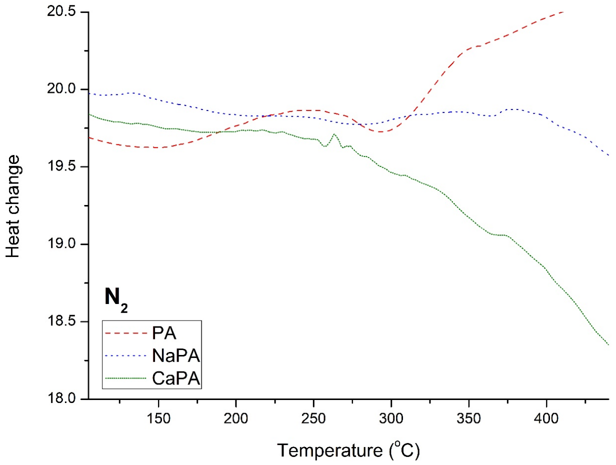

Figure 20. DSC curves of pure flame retardants. Red: $H_{12}PA$, Blue: Na_6H_6PA, Green: Ca_4H_4PA.

DSC curves of the pure flame retardants are shown in Figure 20. $H_{12}PA$ degrades endothermically while Na_6H_6PA and especially Ca_4H_4PA decompose exothermically. There are no similarities between the behavior of the pure flame retardants compared to cotton and sawdust samples treated with these flame retardants (Figure 18 and Figure 19).

The heating rate in TGA experiments were 20°C/minute and in DSC it was 10°C/minute, which can give slightly different temperatures for the processes taking place.

4.5.3 Bomb calorimetry

The bomb calorimetry measurements give a mean value of 19.5±0.4 MJ heat released per kg sample during the complete combustion of untreated sawdust compared to 18.3±0.3 MJ/kg for sawdust treated with $Fe_{0,3}H_{11}PA$-1%, 17.9±1.4 MJ/kg for sawdust treated with $Al_{0,3}H_{11}PA$-3%, and 17.0±1.5 MJ/kg for sawdust treated with Na_6H_6PA-3% [35].

Thus, less heat seems to be released when the sawdust is treated with flame retardants. However, as has been noticed earlier, the amount of flame retardant adsorbed could not be reliably estimated so for the calculations it was assumed that all the mass was wood, which introduces a small error in the calculations. Nevertheless, it is clear that the flame retardants, especially Na_6H_6PA-3%, can have a cooling effect on the combustion process.

4.5.4 Cone calorimetry

In the cone calorimeter, the untreated reference sample took more than 30 seconds to ignite, while the treated samples took only 15-20 seconds to ignite, depending on the flame retardant used, see Figure 21.

On the other hand, once ignited, the untreated sample burnt completely without a stop, while all the treated samples self-extinguished, leaving nearly one third of the original sample weight. The burnt materials still had fairly good mechanical properties; although they became black, they were not completely fragile and could not be torn easily, see Figure 22 for a representative example of what the samples looked like.

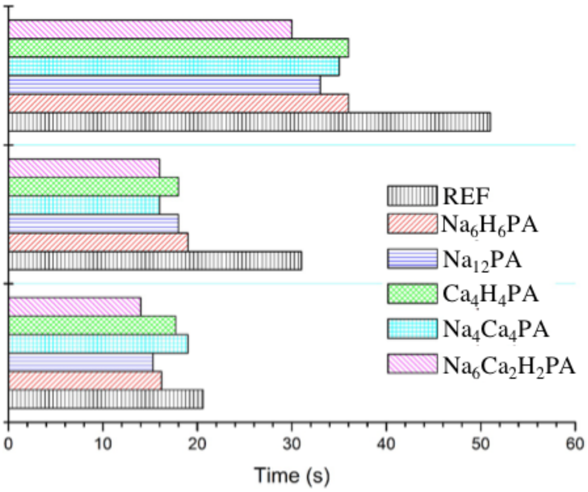

Figure 21. Comparison of time to flameout (top), time to ignition (middle), and time of burning (bottom) for different samples.

Figure 22. Cotton samples after cone calorimeter measurements. Left: Untreated. Right: Na_6H_6PA flame retardant.

The results of the cone calorimeter tests are in accordance with our TGA experiments [33,36], where the effect of flame retardants on the cotton samples were investigated, see Figure 11 for a few examples. The mass loss of the treated cotton samples began at lower temperatures (around 225°C) compared to the untreated sample (around 350°C). When the temperature of the sample reached 375 °C, 85-90% mass loss has already occurred for the untreated sample, while almost 50% of the mass is still left for the treated samples.

Figure 23 shows the heat release rate (HRR) and the total heat released (THR) from the samples compared to the untreated reference sample. The curve resembles the curve shape characteristic for char forming samples [42]. It is encouraging to see that the peak HRR (pHRR) for cotton treated with Na_6H_6PA-3% is nearly half of that for the untreated sample. The THR of the sample is lower than all other samples. In fact, all the sodium containing samples (except Na_4Ca_4PA) have low HRR and THR.

Presence of ionizable protons in Na_6H_6PA and $Na_6Ca_2H_2PA$ causes faster charring of the sample surface, forming a barrier which effectively stops further spreading of fire inside the sample.

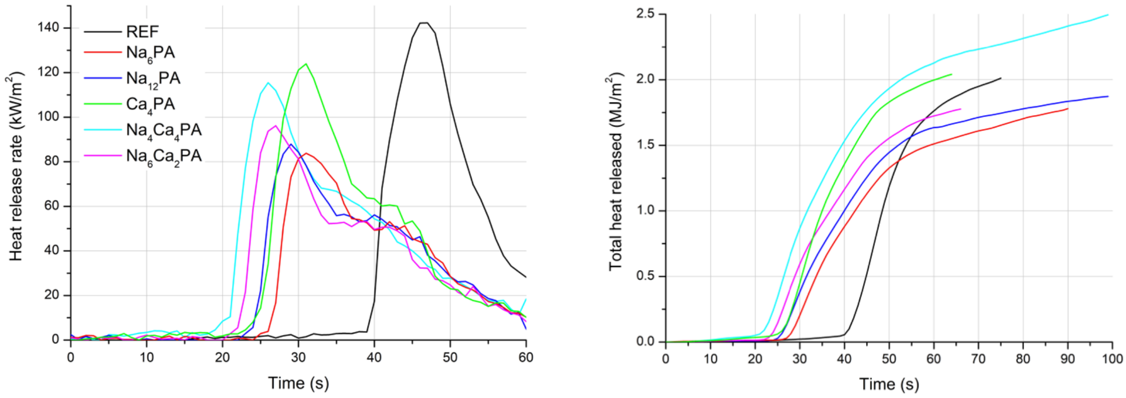

Figure 23. Cone calorimeter tests on cotton samples treated with different flame retardants. Left: HRR. Right: THR.

Na_4Ca_4PA is less effective because there are no ionizable protons in that compound so no phosphoric acid can form and no charring can occur. Here, the only flame retarding mechanism is the barrier formed by the flame retardant coating itself. $Na_{12}PA$ also does not have ionizable protons, but presence of high number of sodium atoms makes it a fairly good flame retardant.

Ca_4H_4PA has ionizable protons, but still has the worst performance of the flame retardants. Here it can be speculated that the stronger bonds between calcium and phosphate, compared to sodium and phosphate, hinders the efficient formation of phosphoric acid, but it can also be that the sodium has a radical quenching effect in this case [14,15].

As mentioned, the HRR is much lower for sodium based samples and are in the order Na_6H_6PA < $Na_{12}PA$ < $Na_6Ca_2H_2PA$, while the total time of burning for treated cotton with these three compounds is in the opposite order. The low HRR and short time to ignition causes the sample to catch fire at a lower temperature, but also to self-extinguish at a lower temperature. The peak temperature of the flame will be colder for these samples compared to the untreated one. This lower temperature will also ensure less release of flammable gases, which occurs when the sample reaches higher temperature [6].

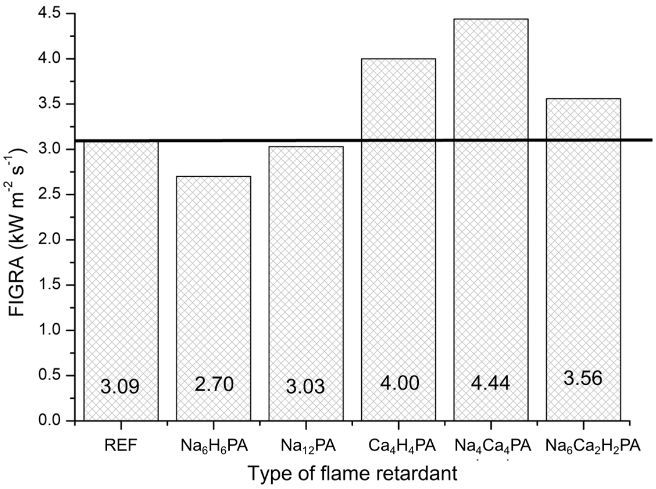

Figure 24. FIGRA index for cotton samples treated with different flame retardants.

Figure 24 shows FIGRA index of the samples. The graph shows that all the treated samples have comparable FIGRA index to the untreated reference material. Na_6H_6PA and $Na_{12}PA$ samples, which have only sodium atoms, have slightly better FIGRA index compared to the reference material.

The cotton used was very thin. A thicker material may be able to form a thicker layer of char that will work as a fire-insulating barrier and protect the underlying material better. That would improve the FIGRA index.

4.6 Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR)

4.6.1 Pure flame retardant complexes

Figure 25 shows what happens to the carbon atoms in Ca_4H_4PA and Na_6H_6PA when heated to different temperatures. At 200°C, no decomposition has begun and the carbon ring in PA is intact. This is shown by the fact that there is a signal at about 70 ppm which is the typical range for C-H bonds [43] found in the phytic acid ring (recall Figure 1).

At 300°C, no signal is left from Na_6H_6PA at 70 ppm, but two new signals have appeared around 120 ppm and 150 ppm. These are typical signals for aromatic compounds [44]. When the phosphate groups break away from the hydrocarbon ring in the phytic acid, it is aromatized so that the original hydrocarbon ring now becomes an aromatic ring, a sign of charring. When carbon compounds are charred, hydrogen atoms break away from the structure and new bonds are created between the carbon atoms. These aromatic rings are then bonded together as the charring proceeds and more and more hydrogen is removed. The higher the charring rate, the greater the C:H ratio and the larger polyaromatics are formed. If oxygen is not available for combustion, then a graphite-like material can eventually be formed.

According to the ^{13}C NMR data, Ca_4H_4PA is more stable than Na_6H_6PA since the original signal around 70 ppm is still left at 300°C in parallel with the aromatic signals. At 400°C, Ca_4H_4PA has also been fully aromatized. At 600°C, the signal strength has decreased, i.e. a smaller amount of polyaromatics is left as the sample residue slowly smoulders, and at 800°C the amount of carbon is no longer detectable. TGA results in air (Figure 17), show that the main mass loss, the polyaromatization, occurs more or less at the same temperature for Ca_4H_4PA and Na_6H_6PA, but the mass loss starts at a lower temperature for Na_6H_6PA.

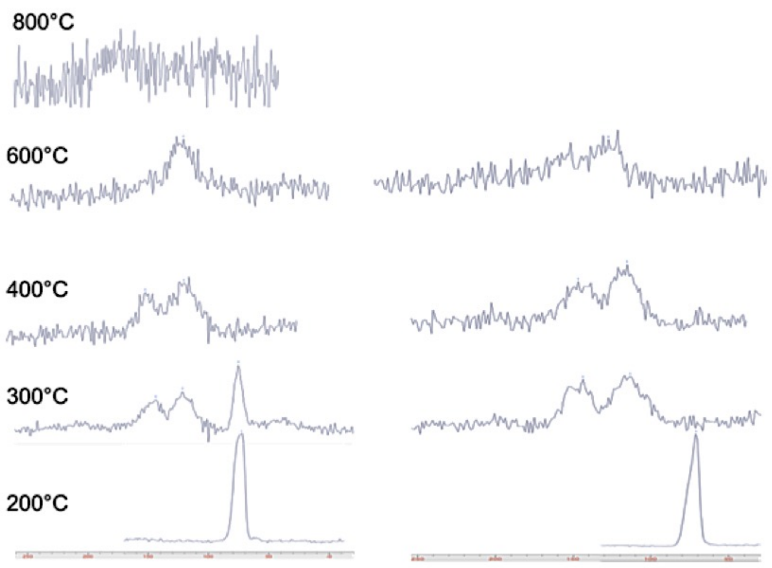

Figure 25. ^{13}C NMR spectra of Ca_4H_4PA (Left) and Na_6H_6PA (Right) heated to different temperatures. The y-axis is not to scale.

$H_{12}PA$ (not shown in Figure 25) has aromatized completely and partly burnt already at 300°C, leaving only a weak signal in the ^{13}C NMR spectrum. TGA in air (Figure 17) shows that $H_{12}PA$ starts to decompose and char below 300°C, although the main mass loss occurs at around 350°C. Thereafter the remaining charred material (50% of the original mass) slowly smoulders.

Figure 26 shows what happens with the phosphorus atoms in Ca_4H_4PA and Na_6H_6PA when heated to different temperatures. At 200°C one signal is at the original position around 0 ppm shift [45] from concentrated phosphoric acid, which is used as the reference compound, and another signal is to the right of the original signal (around -10 ppm). At higher temperatures, the peaks further shift position and appearance, indicating that something is happening to the flame retardant.

It is known that when phosphates polymerize into polyphosphates, the peaks shift to the right in the spectrum [34,46]. The higher the degree of polymerization, the more the peaks are shifted to the right. Thus, from Figure 26 it can be seen that the flame retardants have started to polymerize already at 200°C, forming pyrophosphates [46-48].

Based on the relative heights of the peaks, Ca_4H_4PA (peak area ≈ 1:1) has a relatively higher amount of polymerized material (≈50%) than Na_6H_6PA (peak area ≈ 3:1) (≈25%). Interestingly, the ^{13}C NMR spectra at 200°C (Figure 25) show no sign of degrading of the hydrocarbon ring.

Na_6H_6PA has polymerized completely at 400°C (no signal left around 0 ppm), and has started to form linear and cyclic polyphosphates and metaphosphates, the larger the number of phosphates in the chain or ring, the more the signal has shifted towards the right. Surprisingly, at 600°C the degree of polymerization has lowered (the rightmost peak has almost disappeared), and the material has become more well-ordered (narrow peaks rather than a broad peak). According to Figure 25, the remaining char has burnt completely above 600°C (no carbon atoms left that can give a signal in the spectrum) and possibly this facilitates the ordering of the phosphate part of the flame retardant. At 1000°C, the material has become amorphous again, and is a mixture of linear, cyclic, and branched, three-dimensional phosphate structures. The material may have melted at this temperature, and the fast cooling when the material is taken out of the furnace has left it in an amorphous glassy state (see Figure 5).

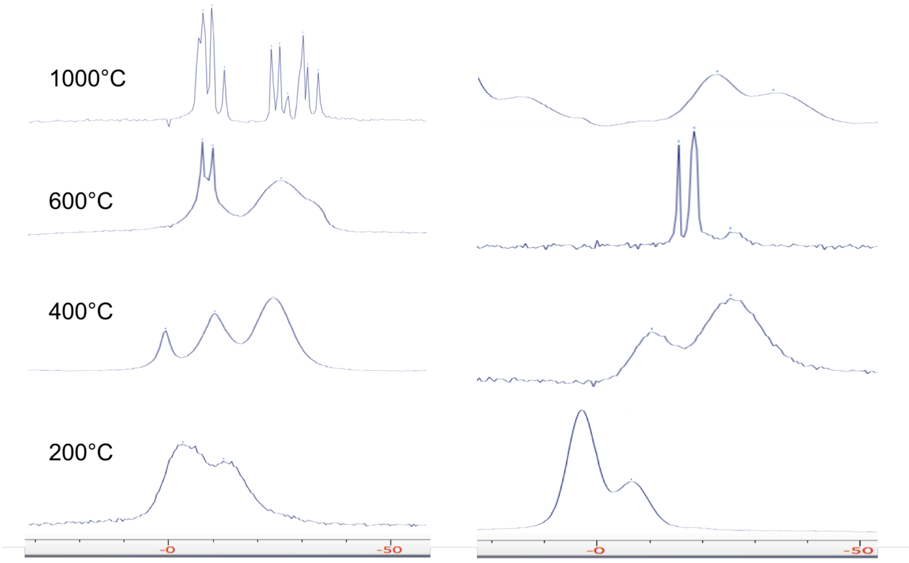

Figure 26. ^{31}P NMR spectra of Ca_4H_4PA (Left) and Na_6H_6PA (Right) and heated to different temperatures. The y-axis is not to scale.

At 400°C, Ca_4H_4PA has formed three types of phosphates; a small amount of enamel-like calcium phosphate (the peak that has shifted to the left) [45,49], and two types of linear and/or cyclic polyphosphates of varying degrees of polymerization. At 600°C, the enamel-like calcium phosphate is gone (the leftmost signal has disappeared), a fraction of the sample has become well-ordered, and the phosphate groups have started to form three-dimensional network structures (a small peak furthest to the right). The many narrow signals at 1000°C means that the material has become highly crystalline.

$H_{12}PA$ (not shown in Figure 26) shows no signs of polymerization at 300°C. At 400°C, a small amount of linear or cyclic polymers have started to form, and at 700°C, there is still some $H_{12}PA$ left, and some three-dimensional polyphosphate networks have formed, but most of the sample is linear or cyclic polymers [34].

Polymerisation of phosphates is an endothermic process, giving away water vapor which can cool and dilute combustible vapors. The polyphosphates seem to be very stable and thus, can form a barrier, preventing combustible gases from an underlying material to come into contact with air. The early onset of high polymerization of Na_6H_6PA, can explain its relatively good performance as a flame retardant, assuming that the decomposition mechanism is the same when the flame retardant is in contact with cotton or wood. The polymerization cannot start before the PA has decomposed and released the phosphate fragments. Thus, early decomposition of the flame retardant releases phosphoric acid which chars the surface. As previously mentioned, early charring leads to a pyrolysis mechanism giving less combustible gases [8,32]. Thereafter, the phosphates polymerize, which contributes with cooling and dilution by water vapor. The polymerization can also have a radical quenching effect [16]. The stable polyphosphate then acts as a second protective barrier above the charred layer. The gases formed leads to an intumescence of the material (see Figure 5), and whether this affects the heat conducting properties of the material has not been studied here. It is also worth mentioning, that sodium can in some cases have a radical quenching effect [14,15]. For this to happen, NaOH molecules must form in the vapor phase.

TGA and DSC curves for the pure flame retardants (Figures 17 and 20), show that the initial mass loss of $H_{12}PA$ starts below 200°C and is endothermic. The main loss after 300°C is also endothermic. The decomposition of Na_6H_6PA takes place without almost any heat changes until above 350°C where an exothermic process takes place. Above 400°C, the degree of polymerization has decreased and the sample has become more crystalline (according to Figure 26). The depolymerisation is exothermic, and crystallisations are normally exothermic as well. Ca_4H_4PA has a very exothermic decomposition process after approximately 275°C, the temperature at which the main pyrolysis starts. According to Figure 26, some calcium phosphate has formed, and this is a very stable compound, and possibly releases some energy during its formation, counteracting the energy needed for the polymerization of the rest of the phosphates. In general, calcium ions bind very strongly to the phosphate groups, which may hinder an efficient degrading and also lead to more stable compounds (and exothermic processes taking place).

4.6.2 Cotton samples treated with flame retardants

Figure 27 shows what is happening to the flame retardant on cotton during heating to different temperatures. In order to run ^{31}P MAS NMR, the sample has to be easy to pack tightly inside the rotor. Otherwise it will not be possible to spin the sample at the high speeds needed (at least 10 kHz spinning frequency). The cotton samples had not decomposed enough below 450°C to be able to pack them properly, so no data is available for lower temperatures at the moment.

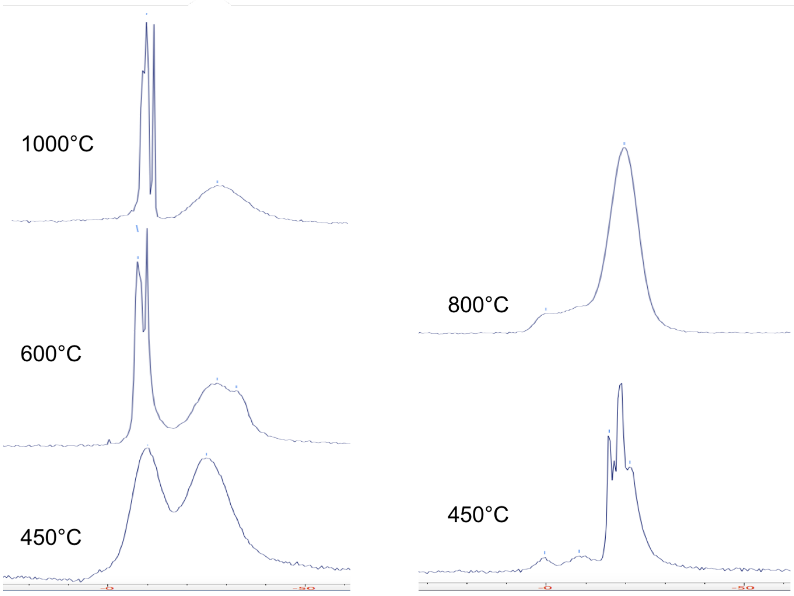

Figure 27. ^{31}P NMR spectra of cotton samples treated with Ca_4H_4PA-3% (Left) and Na_6H_6PA-3% (Right) and heated to different temperatures. The y-axis is not to scale.

The Ca_4H_4PA flame retardant on cotton has polymerized at 450°C, and becomes more crystalline at 600°C. The results are very similar to the ones from the pure flame retardant, but the sample at 1000°C is less crystalline.

At 450°C, the Na_6H_6PA flame retardant on cotton has formed a small amount of pyrophosphate, but the bulk of the sample is highly polymerized, and crystalline. At 800°C, the sample has become amorphous again.

TGA curves of the same samples in air (Figure 12) correlate well with the NMR data. Pyrolysis and charring has occurred before 450°C. Cotton treated with Na_6H_6PA has more mass left at this temperature, compared to cotton treated with Ca_4H_4PA. The polymerized phosphates have formed longer chains and larger rings from Na_6H_6PA than from Ca_4H_4PA, which gives a more efficient additional barrier. Possibly, it is easier to polymerize Na_6H_6PA than Ca_4H_4PA because of the weaker bonds between sodium and phosphate compared to calcium and phosphate.

The cone calorimetry data (Figure 23) showed that Na_6H_6PA was a better flame retardant than Ca_4H_4PA. The faster the PA can decompose and form phosphoric acid, the faster the charring of the cellulose can start, and the prevention of fire will be more efficient.

4.6.3 Wood samples treated with flame retardants

Figure 28 shows what is happening to sodium phytate flame retardants on sawdust (spruce) during heating to different temperatures. In the spectrum of $Na_{12}PA$ (left), the peaks shift towards the left during heating. No polymerization occurs. At 1000°C, the sample mostly consists of sodium phosphate. In the spectrum of Na_6H_6PA (right), the peaks shift towards the right during heating. Above 400°C, the bulk part of the sample polymerizes and crystallizes. No polymerization can occur when there are no available hydrogens in the sample ($Na_{12}PA$). Compared to the pure flame retardant (Figure 26), the sawdust delays the polymerization of Na_6H_6PA, so that it does not take place until above 400°C. Once the polymerization takes place, it becomes more extensive, forming larger polyphopshates.

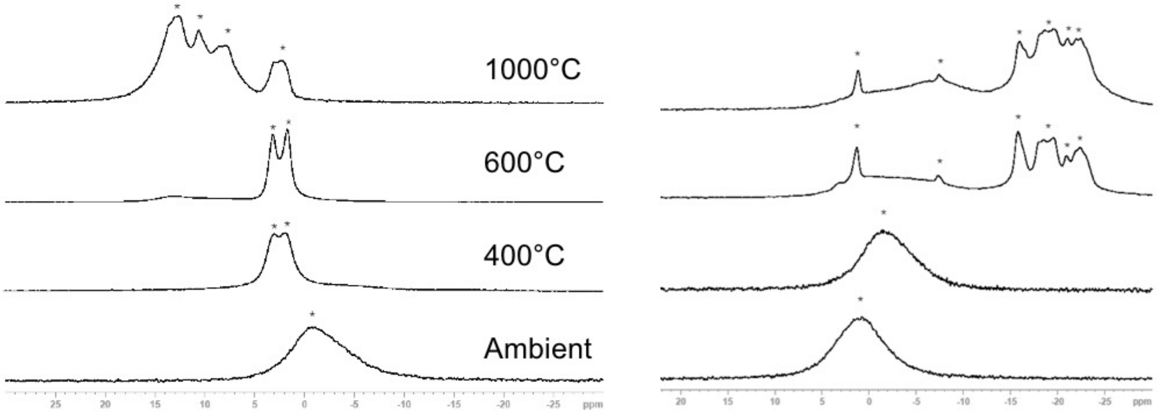

Figure 28. ^{31}P NMR spectra of sawdust (spruce) treated with $Na_{12}PA$-3% (Left) and Na_6H_6PA-3% (Right) and heated to different temperatures. The y-axis is not to scale. Edited from [34].

Ca_4H_4PA on sawdust polymerizes above 400°C, but the polymers are small, only a few phosphates per molecule [34].

5 Conclusions and recommendations

By combining different chemical analysis methods, we can describe what happens to phytic acid-based flame retardants during the thermal decomposition process. The results from the different methods agree with each other, and the complementary information given from each of them builds a more complete picture. The molecular level analysis on small scale samples can be linked to the macroscopic fire properties.

The main focus has been on cotton as there were several experimental difficulties with wood (e.g. leaching of minerals, and changes in humidity), but nevertheless, the results attained for wood samples are very similar to those for cotton.

Phytic acid itself shows the best flame retarding performance in simple combustion tests. However, the acid itself has very low pH so it deteriorates cotton, so no further investigations have been done on this. Sodium-based flame retardants have a higher pH and seems to not damage the cotton. The sodium phytates have almost as good performance as the pure acid, even at low concentrations. At higher concentrations of flame retardants, the performance is even better, but the coating makes the material stiff and uncomfortable. The sodium phytates are water-soluble, but water-resistance can be obtained through calcium ions which form a dense and difficult to dissolve enamel-like surface layer which also acts as a barrier to separate fuel from oxygen. However, the calcium-based flame retardants are not as good as the sodium versions.

Iron and aluminium phytates are also water-resistant, and the studies indicate that they may have good function as flame retardants, but they are so insoluble in water that it was difficult to put high concentrations of the metals on the wood samples with the coating method used. This problem can be overcome by dipping in separate solutions.

Phosphorus-based flame retardants work by charring at low temperatures (before main degradation of the cellulose), which leads to reduced fuel production. The phosphates in the flame retardant polymerizes, which has a cooling effect and forms a protective barrier.

Cotton samples self-extinguish in the cone calorimeter, even at a very low amount of flame retardant and the HRR is lower than for untreated cotton. FIGRA index is lower than the reference sample for the sodium phytate flame retardants, but higher for the calcium phytates.

Due to the ionic character of the phytates, the flame retardant coating became hard and made the textile a bit stiff. By keeping the pH of the solution not too low, the cotton itself seems to not be damaged, so by modifying the ionic properties of the coating it can be made more flexible. Continued investigations on how coating composition and application procedures are affecting the properties of cellulose-based textile materials are needed.

Further studies are needed on wood as well, to assess the flame retarding properties fully on that material. On wood, a thicker coating can be applied without negative effects, as wood is a stiff material in itself, so the flame retardant will give the same effect as a paint or lacquer. With a thicker coating, the intumescent effect seen for the pure phytate complexes, can be investigated. It is also possible to investigate the use of wood chips treated with phytate flame retardants to make particle boards.

An efficient methodology is now developed where different flame retardants can be systematically screened for adsorption capacity on a material, thermal properties, thermal degradation mechanisms, and water solubility, to pick suitable candidates for larger scale tests and tests according to standards.

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Appendix

Appendix 1 Preparation of solutions

Chemicals

Aqueous solution of phytic acid (50% w/w): $C_6H_6(H_2PO_4)_6$ or $H_{12}PA$
Sodium hydroxide pellets: NaOH
Calcium hydroxide: $Ca(OH)_2$
Aqueous solution of ammonia (25% w/w): NH_3
Calcium chloride hexahydrate: $CaCl_2 \cdot 6H_2O$
Iron(III) chloride hexahydrate: $FeCl_3 \cdot 6H_2O$
Aluminium chloride hexahydrate: $AlCl_3 \cdot 6H_2O$

Solutions

3% phytic acid solution was made by diluting 6 grams of 50% $H_{12}PA$ in water to 100 g volume. The solution is called $H_{12}PA$-3% in the report.

10% phytic acid solution was made by diluting 20 g 50% $H_{12}PA$ in water to 100 g volume.

1% phytic acid solution was made by diluting 2 grams of 50% $H_{12}PA$ in water to 100 g volume.

To the phytic acid solutions, the proper amount of different chemicals were added according to Table 1A. For more details, see the references [29-32]. The formulae give approximate molar ratios between phytic acid and additive. One mole phytic acid ($H_{12}PA$) has in total 12 H^+ which can be replaced by different ions.

Table 1A. Flame retardant solutions used in the study.

Additive	Formula	Comment
NH_3	$(NH_4)_{12}PA$	3% and 10%
NaOH	Na_6H_6PA	3% and 10%
NaOH	$Na_{12}PA$	3% and 10%
NaOH + $CaCl_2$	$Na_4Ca_2H_4PA$	Only 3%
NaOH + $CaCl_2$	Na_4Ca_4PA	3% and 10%
NaOH + $CaCl_2$	$Na_6Ca_2H_2PA$	3%
$CaCl_2$	Ca_4H_4PA	3% and 10%
$CaCl_2$	Ca_6PA	Only 3%
$Ca(OH)_2$	$Ca_{0,5}H_{11}PA$	Only 3%, higher $Ca(OH)_2$ gave precipitation
$FeCl_3$	$Fe_{0,3}H_{11}PA$	Only 1%, higher concentration of PA and larger amount of Fe^{3+} gave precipitation
$AlCl_3$	$Al_{0,3}H_{11}PA$	Only 3%, larger amount Al^{3+} gave precipitation

The reactions taking place are assumed to go to completion and are as follows:
$12NH_3(aq) + H_{12}PA(aq) \rightarrow (NH_4)_{12}PA(aq)$
$6NaOH(aq) + H_{12}PA(aq) \rightarrow Na_6H_6PA(aq) + 6H_2O(l)$
$12NaOH(aq) + H_{12}PA(aq) \rightarrow Na_{12}PA(aq) + 12H_2O(l)$

$4NaOH(aq) + 2CaCl_2(aq) + H_{12}PA(aq) \rightarrow Na_4Ca_2H_4PA(aq) + 4H_2O(l) + 4HCl(aq)$

$4NaOH(aq) + 4CaCl_2(aq) + H_{12}PA(aq) \rightarrow Na_4Ca_4PA(aq) + 4H_2O(l) + 8HCl(aq)$

$6NaOH(aq) + 2CaCl_2(aq) + H_{12}PA(aq) \rightarrow Na_6Ca_2H_2PA(aq) + 6H_2O(l) + 4HCl(aq)$

$4CaCl_2(aq) + H_{12}PA(aq) \rightarrow Ca_4H_4PA(aq) + 8HCl(aq)$

$6CaCl_2(aq) + H_{12}PA(aq) \rightarrow Ca_6PA(aq) + 12HCl(aq)$

$0{,}5Ca(OH)_2 + H_{12}PA(aq) \rightarrow Ca_{0,5}H_{11}PA(aq) + H_2O(l)$

$0{,}3FeCl_3(aq) + H_{12}PA(aq) \rightarrow Fe_{0,3}H_{11}PA(aq) + HCl(aq)$

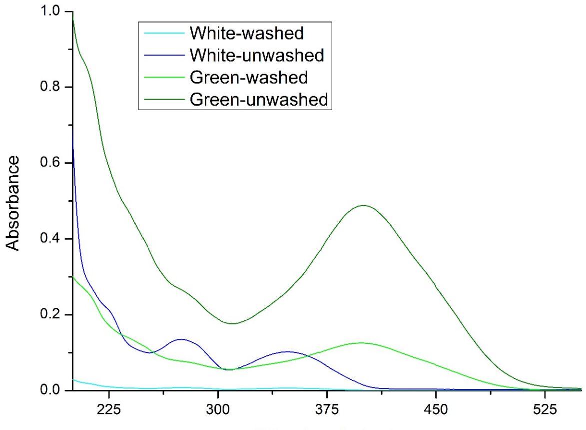
$0{,}3AlCl_3(aq) + H_{12}PA(aq) \rightarrow Al_{0,3}H_{11}PA(aq) + HCl(aq)$

Appendix 2 Analysis of dye content in cotton fabrics

The cotton fabrics used in this study were standard 100% cotton from a common dealer.

Cotton pieces (green and white color) were dipped in water for 24 hours and the UV-Vis spectra of the resulting solutions were recorded (Figure 1A). It was found that they all leach more and more colors with increasing dipping time. The solution resulting from white cotton absorbs below 400 nm, so no color is visible to the naked eye. Thus, even the white cotton is not 'pure' cotton or 'colorless' cotton (though the cloth dealers claim it to be 'totally untreated').

Thus, it appears that the white cloth is almost dye-free after washing, but it was also checked that the white unwashed cloth does not contain any optical whiteners or bleachers (added to give the cloth a whiter appearance). Because the bleaching chemicals can be oxidizing they can enhance the fire properties. The white unwashed cloth was dipped for 24 hours in water, and a few drops of the leachate were added to acidified potassium iodide solution, in contact with chloroform. If an oxidizer is present in the leachate, the iodide ions will be oxidized into elemental iodine, which will give a violet color to the chloroform layer. No coloration was observed in the chloroform layer, so no bleach was present. There was no significant effect on burning behavior between colored and white fabrics, as we found.



Figur 1A. UV-Vis spectra of cotton dipped in water for 24 hours.

Appendix 3 UV-Vis calibration

Phytic acid (PA) itself has very low absorbance so direct measurements of the UV-Vis signal requires very large amounts of PA to be detectable, see Figure 2A Left. In order to detect small concentrations of PA, the indirect method of using iron(III) thiocyanate was used, see Figure 2A Right. A calibration curve was set up by putting 8.1 mg of $FeCl_3 \cdot 6H_2O$ in a 100 ml volumetric flask and adding 50 mg of NH_4SCN and 8 ml of concentrated HNO_3 to it. Water was then added up to the mark.

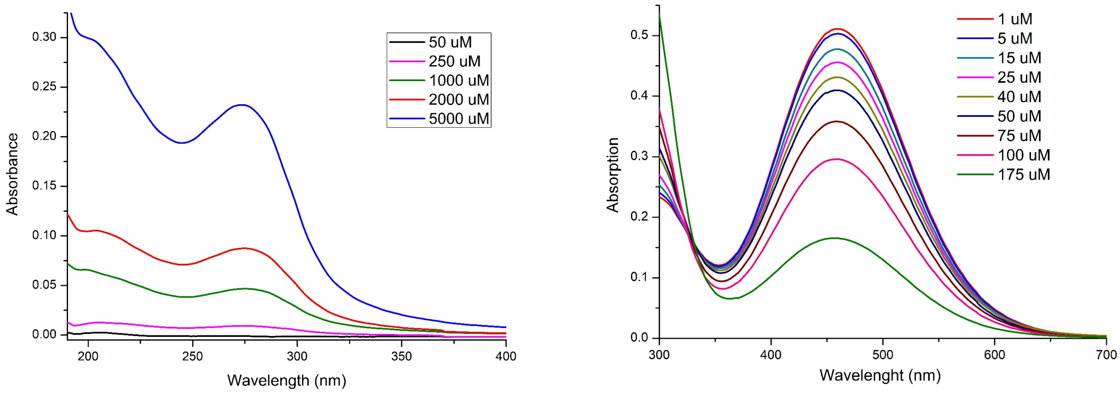


Figure 2A. Left: UV-Vis absorption spectra of various concentrations of phytic acid itself. Right: UV-Vis absorption spectra of various concentrations of phytic acid after complexation with excess iron(III) thiocyanate.

2.5 ml of the prepared 300 μM solution was transferred to a cuvette. 0.5 ml of PA solution (of various known concentrations) was added to it and mixed well. PA forms very stable complexes with Fe^{3+} so the UV signal from $Fe(SCN)_3$ will decrease the higher the concentration of PA is present in the solution. Figure 3A shows the calibration curve that was given from the absorbance data in Figure 2A (Right).

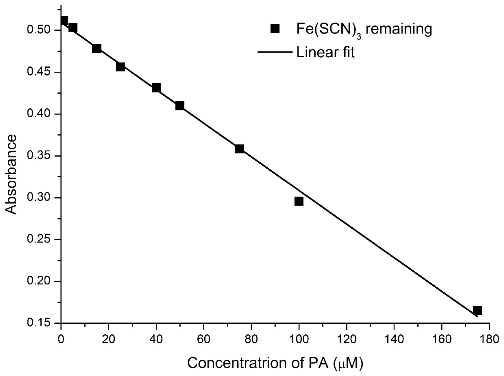


Figure 3A. Absorbance vs concentration plot (Lambert-Beer law).

The concentration of PA in an unknown sample can then be determined from the calibration curve by reading the absorbance from the sample.

The $Fe(SCN)_3$ solution is stable for at least one day at room temperature.

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